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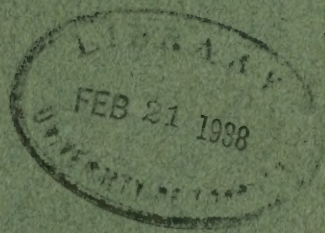
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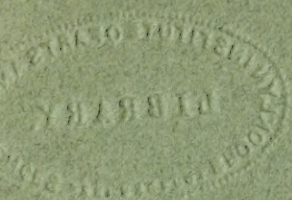
FREDERICK G. COTTRELL, DIRECTOR

THE MANUFACTURE OF SULPHURIC ACID
IN THE UNITED STATES

BY

A. E. WELLS and D. E. FOGG





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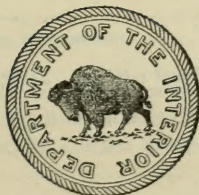
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THE MANUFACTURE OF SULPHURIC ACID IN THE UNITED STATES.

By A. E. WELLS and D. E. FOGG.

INTRODUCTORY STATEMENT.

When the United States entered the World War governmental agencies found little definite knowledge available as to the exact capacity of each sulphuric acid plant in the United States to manufacture acid under the stress of a great emergency. It is true that on account of the demand for acid for the manufacture of munitions for the Allies, prior to the entrance of this country into the war, most of the acid plants near industrial centers in the Eastern and Northern States were running at or nearly their maximum capacity, but, for various reasons, many plants in these States and plants in other districts were not.

For a number of years statistics as to the production of acid by the plants of the country were compiled by the United States Geological Survey, but obviously such figures did not give information as to the maximum capacities that might be available for meeting the heavy war requirements, or as to the steps that would have to be taken to bring these capacities into use.

During the summer and early fall of 1917 various attempts were made to obtain the desired information, but no satisfactory or complete data were obtained. Late in 1917, under the authority granted to the Bureau of Mines by the explosives act, the Director of the Bureau of Mines directed A. E. Wells, metallurgist of the bureau, to make a complete survey of the situation. Mr. Wells personally conferred with officials of the acid companies and visited most of the acid plants in the North that are east of the Mississippi River. The information obtained through this personal survey, together with that obtained through the ready cooperation of the subcommittee on acids, and the subcommittee on fertilizers of the Committee on Chemicals of the Council of National Defense, enabled the preparation of a report containing the desired data concerning the sulphuric acid industry. This report was made immediately available to the War Industries Board and to those offices in the War and Navy Depart-

ments that were most directly concerned in planning the explosives program and in obtaining the necessary supplies to produce the explosives.

Beginning with this survey and report, the sulphuric acid section of the war minerals investigations of the Bureau of Mines took an active part in all matters pertaining to the sulphuric acid industry during the remainder of the war. Mr. Wells, the chief of the section, was appointed an associate chief of the sulphur, pyrite, and sulphuric acid sections of the War Industries Board. Also, by this direct contact with the War Industries Board, the data obtained by Messrs. R. R. Hornor, H. A. Buehler, and O. Lindstrom, who were in charge, for the bureau, of the investigations concerning the supplies of pyrite and sulphur, were constantly made available to all interested Government agencies. D. E. Fogg, of New York City, was appointed chemical engineer to the sulphuric acid section to make special investigations relating to the acid industry, especially the possible utilization, in an emergency, of those sources of raw material not then being used. Mr. E. E. Corbett, of Brooklyn, N. Y., was appointed chemical engineer to make investigations concerned primarily with the conservation of acid. Direct and intimate contact with the industry was had through the close cooperation with the committee on acids of the Chemical Alliance, this committee during the greater part of 1918 occupying rooms with the acid section of the bureau.

With the ending of the war and the close of the active work of the acid section of the bureau, the suggestion was made by many interested parties that a bulletin be prepared giving some of the fundamental and most important facts regarding the sulphuric acid industry, including a discussion of the technical features of the manufacture of acid. During the war the bureau received a vast number of inquiries in regard to various phases of the industry, and this fact also made such a bulletin seem desirable.

Therefore, the present bulletin was prepared to cover the main facts in regard to the industry in this country, including a discussion of the supplies of sulphur-bearing raw materials, the situation of the acid plants, the principal points in regard to manufacturing processes, and the uses of the acid. No attempt has been made to discuss at length the manufacturing processes, as details differ more or less at the different plants and in general are carefully guarded by the acid companies. A great deal of the data given in this bulletin may be found in various publications, but this is the first publication in which such data have been assembled and made readily available. Most of the data were obtained directly from observation and from cooperating acid companies or from individuals who had

been or are now engaged in acid manufacturing and were liberal and generous in making their information available for publication. Care has been exercised to publish no data that were obtained as confidential by the bureau's representatives.

The average acid manufacturer may be already more or less acquainted with most of the information presented in this bulletin, yet it is believed that the bulletin will be of value to those who wish to obtain a general review of the present condition, both the economic and technical, of the sulphuric acid industry in the United States.

ACKNOWLEDGMENTS.

The authors wish to acknowledge the kind courtesies and cooperation of the many men connected with the acid industry who furnished information for the purpose of assisting the work of the bureau in its efforts to serve the country and for aiding the preparation of this bulletin.

Special acknowledgment is made of the valued cooperation of the following men: Mr. Peter Gilchrist, of the Chemical Construction Co.; Mr. Paul Webster, of the Kalbperry Corporation; Mr. A. D. Ledoux, of the Pyrites Co. (Ltd.); Mr. W. D. Huntington, of the Davison Chemical Co.; Mr. A. B. Baker, formerly a lieutenant of the Ordnance Department of the Army, now with J. T. Baker Bros.; Mr. E. L. Larison, superintendent of the acid plant of the Anaconda Copper Mining Co.; members of the Research Corporation; Chas. H. MacDowell, president of the Armour Fertilizer Works; and Mr. M. F. Chase, consulting engineer.

In the preparation of the report use has been made of data concerning pyrite and sulphur supplies obtained by Messrs. R. R. Horner, H. A. Buehler, and O. Lindstrom.

GENERAL REVIEW OF THE SULPHURIC ACID INDUSTRY.

Sulphuric acid is one of the most important of all chemicals, not only because of the large quantities manufactured, but also because of the wide use of the acid in many different industrial works. Sulphuric acid is to the chemical industry what iron is to metallurgy. The general public, however, does not realize this fact, for sulphuric acid does not appear in the finished product as does iron or steel, but is only an intermediate raw material, or is only a means to an end. It is essential in many industries, such for example, as in the manufacture of phosphate fertilizers, explosives, dyes, petroleum products, of various acids other than sulphuric, of ammonium sulphate, aluminum sulphate, and innumerable other chemical and metallurgical products. In recent years in the United States, especially in the East, the demand for sulphuric acid for chemical and metallurgical industries has been an accurate and sensitive barometer of the general business conditions. This demand for acid responds much more quickly to a general slump or boom in the industrial world than does the demand for iron and steel.

The basis for the commercial manufacture of sulphuric acid in this country is the conversion of sulphur dioxide (SO_2) to sulphur trioxide (SO_3) and the uniting of sulphur trioxide with water (H_2O) to form the acid (H_2SO_4). The sulphur dioxide may be formed by burning brimstone, or by burning iron pyrites, and various other metallic sulphides. The reactions involved in the manufacture of the acid are brought about by two processes—the chamber process and the contact process, both of which will be generally discussed in the following pages.

NOMENCLATURE OF SULPHURIC ACID.

As the specific gravity of sulphuric acid can be determined more easily than the strength, acid weaker than 93.19 per cent H_2SO_4 is nearly always spoken of and sold as being of so many degrees Baumé, the Baumé hydrometer being the instrument generally used for de-

termining the specific gravity. The following is a list of the principal commercial strengths of acid, showing the values in Baumé degrees and their H_2SO_4 equivalents as agreed to by the Manufacturing Chemists Association in 1882:

Degrees Baumé.	Per. cent H_2SO_4 .
50 -----	62.18
60 -----	77.67
66 (oil of vitriol) -----	93.19

Acids between 93.19 per cent H_2SO_4 and 100 per cent H_2SO_4 are spoken of as so many per cent sulphuric acid, 100 per cent being commonly called monohydrate.

SO_3 dissolves in the monohydrate, giving fuming acid or "oleum." There are three ways of stating the strength of fuming acid: (1) The percentage of free (dissolved) SO_3 ; (2) the percentage of total SO_3 ; (3) the equivalent percentage of 100 per cent H_2SO_4 —that is, the percentage of 100 per cent H_2SO_4 the fuming acid would make if sufficient water were added to combine with all the free SO_3 . For example: Twenty per cent "oleum" would contain 20 per cent free SO_3 and 80 per cent actual H_2SO_4 , or would contain 85.3 per cent SO_3 , and if sufficient water were added to combine with all the free SO_3 the oleum would make 104.49 per cent of H_2SO_4 .

There are a number of books giving formulas and tables for use in sulphuric acid calculations, and data on the physical properties of sulphuric acid. One of the most recent handbooks with such data is that prepared by Sullivan.^a As such complete tables and calculations are already available in the literature few of these data will be duplicated in this bulletin. However, the following conversion factors are given here for the convenience of the reader, who may not have conversion tables at hand:

1. Fifty-degree B. acid ("chamber acid") contains 50.76 per cent SO_3 or 62.18 per cent H_2SO_4 . A stated weight of 50° B. acid multiplied by 0.8 gives the equivalent weight of 60° acid, or multiplied by the fraction $\frac{2}{3}$ gives the equivalent weight of 66° acid.

2. Sixty-degree B. acid contains 63.41 per cent SO_3 or 77.67 per cent H_2SO_4 . A stated weight of 60° acid multiplied by 1.25 gives the equivalent weight of 50° acid, or, multiplied by the fraction $\frac{5}{6}$, gives the equivalent weight of 66° acid.

3. Sixty-six degree B. acid ("oil of vitriol") contains 76 per cent SO_3 or 93.18 per cent H_2SO_4 . A stated weight of 66° acid multiplied by 1.2 gives the equivalent weight of 60° acid, and multiplied by 1.5 gives the equivalent weight of 50° acid.

^a Sullivan, T. J., Sulphuric Acid Handbook, 1918, 239 pp.

GROWTH OF THE SULPHURIC-ACID INDUSTRY IN THE UNITED STATES.

PRODUCTION DURING THE PERIOD 1865 TO 1914.

Notwithstanding the extraordinary consumption due to the demands of the Civil War the production of sulphuric acid in this country in 1865 was only 40,000 tons.^a

The production of acid increased gradually and steadily between 1865 and 1890, as shown by the following figures:^b

Growth in production of sulphuric acid in United States, 1865-1890.

Year.	Production as 50° B. acid (tons).
1865 -----	40,000
1870 -----	105,000
1875 -----	150,000
1880 -----	425,000
1885 -----	600,000
1890 -----	765,000

In the period 1890 to 1905 many new plants were put into operation. In fact, in 1900 and 1901 alone the capacity was increased by 37 new plants, making an additional capacity of between 1,200 and 1,300 tons per day. By 1900 the production was approximately 1,600,000 tons, and by 1905 the production was considerably over 2,000,000 tons annually.

The production increased rapidly during the next four or five years, and by 1909 (according to the census report) had increased to 2,750,000 tons, with a total market value of \$15,174,886.

Beginning with the year 1911 the United States Geological Survey compiled production statistics. The figures are given below:

Quantity and value of sulphuric acid produced in United States, 1911-1918.

Year.	Total production as 50° B. acid. ^a	Total value.
1911.....	2,700,000	\$17,369,872
1912.....	2,950,000	18,338,019
1913.....	3,575,000	22,684,526
1914.....	3,800,000	24,479,927
1915.....	4,170,000	32,657,051
1916.....	6,300,000	73,514,126
1917.....	7,200,000	87,540,181
1918.....	^b 7,450,000	(^c)

^a These tonnages are not exact, because there was some doubt as to the exact strength of certain small quantities of high-strength acid, but are undoubtedly within one-half per cent of the actual tonnages.

^b From the records of War Industries Board.

^c Not determined.

The growth of the acid industry during the year prior to 1914 was due very largely to the growth of the fertilizer business in the

^a Adams, W. H., Pyrites as a material for the manufacture of sulphuric acid: Jour. Anal. and App. Chem., vol. 5, Nov., 1891, pp. 601-615, Dec., 1891, 661-670; vol. 6, Jan., 1892, pp. 9-23; Feb., 1892, pp. 73-82; Mar., 1892, pp. 142-150. Production statistics, pp. 605, 608.

^b Census of Manufacturers, Class 1A—Sulphuric, nitric, and mixed acids: Bull. 92, Bureau of the Census, 1908, pp. 15-24.

South, and to the increased amount of oil refining in the East and North. Ingalls,^a estimated that of the approximately 1,600,000 tons of acid (50° B. basis) made in 1900, 800,000 tons, or nearly 50 per cent, was used in fertilizers, and 320,000 tons, or 20 per cent, was used in oil refining, the remainder, 480,000 tons, being used for pickling steel and for manufacturing other acids and chemical products. The consumption of nearly 500,000 tons for steel pickling and chemical manufacture indicates the rapid growth of these industries in the last decade of the nineteenth century.

By 1914 the production was more than 3,500,000 tons, and of this amount approximately 2,200,000 tons was being used in the manufacture of superphosphate. No data are available as to the disposition of the remainder of this acid to the other industries at that time, but it is estimated that the petroleum industries required about 500,000 tons, the iron, steel, and coke industries about 300,000, domestic explosives about 200,000, and other chemical industries 300,000 tons.

PRODUCTION FROM 1914 TO 1917.

During the last half of 1914 the acid industry in the East was obliged to curtail production, owing to the general upset of conditions in the industries caused by the outbreak of the war. Late in 1914 and early in 1915, however, the Allies began to place heavy contracts for manufactured products and munitions, and the demand for sulphuric acid rose by leaps and bounds. Practically every plant in the East ran at maximum capacity during the period from early 1915 to the time of the signing of the armistice in 1918. During 1915, 1916, and 1917 many new plants were built by private concerns, principally by those concerns engaged in the manufacture of munitions. The production rose rapidly as shown by the preceding table. As the increased demand was primarily for high-strength acid, many of the new plants were for the manufacture of acid by the contact process. Much of the 66° B. acid required was obtained by the concentration of chamber acid, new concentrating apparatus being installed at various chamber plants. The increase in the production of 66° or higher strength acid is shown below:

Production of 66° B. and higher-strength acid, expressed as tons of 100 per cent acid.

Year.	Tons.
1913.	810,000
1914.	720,000
1915.	1,160,000
1916.	1,930,000
1917.	2,100,000
1918.	2,400,000

^a Ingalls, W. R., Production and consumption of sulphuric acid in the United States: Mineral Industry, 1906, vol. 15, p. 705.

THE INDUSTRY IN 1918.

In the late summer and early fall of 1917, when it became evident that it would be necessary to supply munitions to possibly several millions of United States troops in France, the matter of obtaining an adequate supply of sulphuric acid for the production of explosives became of even greater importance. It was necessary for the governmental agencies, especially the War Industries Board, to know the exact manufacturing capacity of the country and which plants were being operated to capacity. This information was to a limited extent obtained through the efforts of the subcommittee on acids, and the subcommittee on fertilizers of the Committee on Chemicals, Council of National Defense. The greater part of the data, however, was obtained by a survey, made late in 1917, by the Bureau of Mines.

As a result of this survey the rate of production of acid during the last quarter of 1917 was determined to be approximately 390,000 tons per month (basis 100 per cent H_2SO_4), or approximately 7,500,000 tons per year (basis 50°B.). In order to obtain this production practically all acid plants were being operated at maximum capacity.

At several of the zinc smelters where acid was being made as a by-product in the roasting of zinc ores, brimstone was being used to supplement the sulphur in the ore, but at most of the zinc plants this was not being done because of the peculiar conditions of the contracts under which the acid was sold. As the urgent need for more acid became apparent, late in 1917, these contracts were altered. From January 1, 1917, to November 11, 1918, at practically all the zinc plants brimstone was used to supplement the zinc ore, and every effort was made to operate the chamber and contact plants to the utmost capacity. The total acid manufacturing capacity on January 1, 1918, with the use of brimstone to supplement ores at the zinc plants, was estimated to be about 427,000 tons per month (basis 100 per cent H_2SO_4), or 8,200,000 tons per year (basis 50°B.). Of this total capacity, 29 per cent was at contact plants and 71 per cent was at chamber plants. The total capacity for the manufacture of 66° acid—that is, the capacity of the contact plants plus the capacity of the plants for concentrating weaker acid by heat—was about 226,000 tons per month.

Later in 1917 it became evident that the above capacity would not be adequate to meet the explosives program, with the contemplated enormous increase in the production of smokeless powder and high explosives. As private concerns were not prepared to build enough additional plants to supply the necessary acid, the War and Navy Departments undertook the construction of Government-owned plants. During the first nine months of 1918 additions were made

to the plants of several explosives companies, and of other smaller producers, also the Government built acid plants at a number of points, so that on November 11, the date of the signing of the armistice, the total actual manufacturing capacity of the country had been increased to 501,000 tons per month (basis 100 per cent H_2SO_4), or 9,600,000 tons per year (basis 50° B).

The Government acid plants comprised 55,000 tons (basis 100 per cent H_2SO_4) of this capacity; the plants of the explosives manufacturers comprised 58,000 tons, and the remainder, 388,000 tons, was the capacity of the plants owned by the commercial manufacturers of fertilizers, chemicals, and metallurgical by-products. Of this total capacity, 40 per cent was at contact acid plants and 60 per cent at chamber plants.

In addition to the above, at the time of the signing of the armistice there was under construction plants which would have had a capacity of about 37,000 tons per month (basis 100 per cent H_2SO_4). These plants were in all stages of construction, from the point of just being started to approximate completion. Work on these plants was immediately discontinued and they are not included in the following discussions.

ZONAL DISTRIBUTION.

In order to show in more detail the manufacturing capacity in different sections of the country, the acid plants have been segregated into six zones, shown on the accompanying map (fig. 1), as follows:

Zone 1.—Includes all of New England, the New York City, Philadelphia, and Baltimore districts, and also all of Virginia.

Zone 2.—Includes all of the State of New York outside of a radius of 50 miles of New York City, all of Pennsylvania except the extreme eastern part—that is, outside of a zone, say, 50 miles west from the Delaware River—West Virginia, Ohio, eastern Kentucky, and lower Michigan.

Zone 3.—Includes western Kentucky and western Michigan, all of Indiana, Illinois, Missouri, Wisconsin, Iowa, and Minnesota. In this district, of course, the acid plants are principally at the zinc plants in Illinois and in the Chicago district. The plant at Argentine, Kans., is included in this zone.

Zone 4.—Includes all the South—that is, south of the southern boundaries of North Carolina, Tennessee, and Arkansas and east of Oklahoma and the Sabine River, Texas.

Zone 5.—Includes all the territory between zones 3 and 4 and the Pacific Coast States, which comprise zone 6.

Zone 6.—Includes the Pacific Coast States.

Although the boundaries of these zones were rather arbitrarily chosen, they are to a considerable degree logical divisions. In zones 1 and 2 the acid is manufactured for a wide variety of purposes,

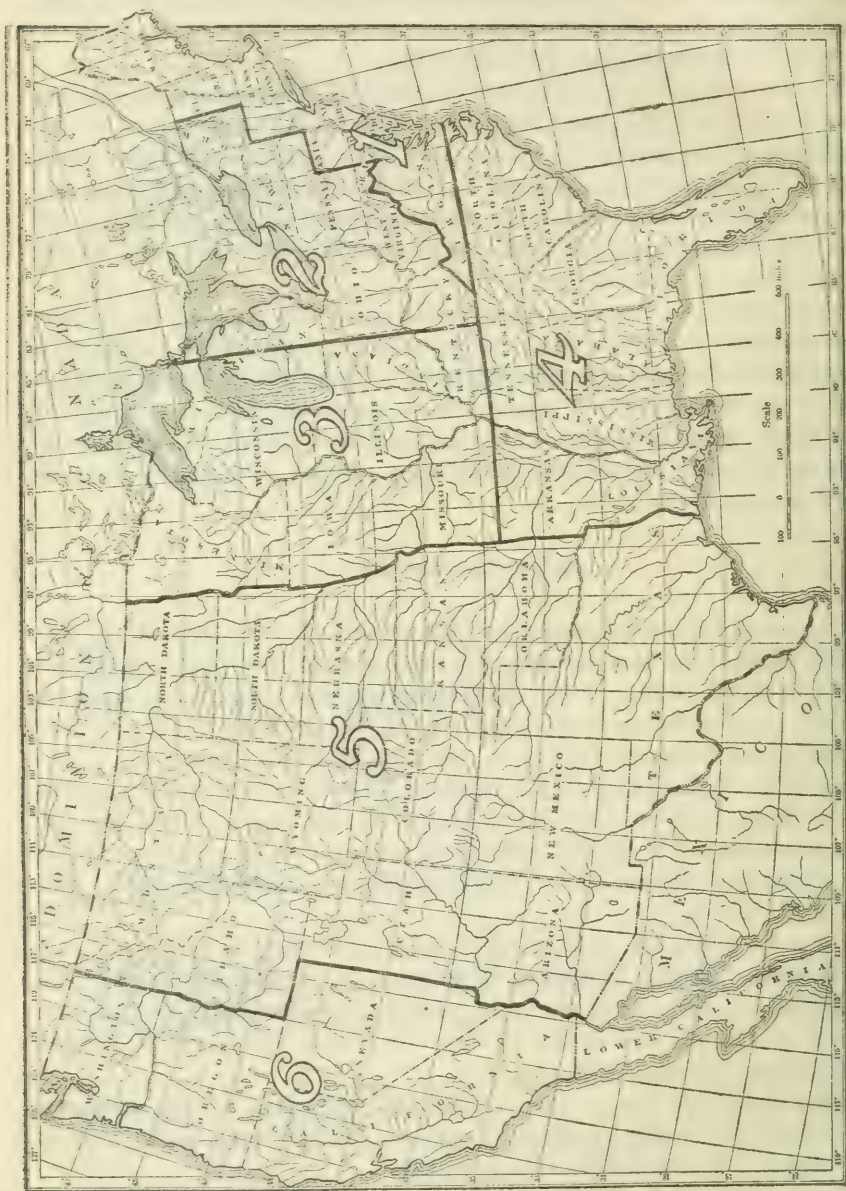


FIGURE 1.—Zones of sulphuric acid manufacture in the United States.

as these zones cover primarily the largest manufacturing centers of the country. In zone 3 the production is essentially a by-product from zinc-smelting operations, although some acid is made by com-

mercial concerns in Chicago and St. Louis. The production in zone 4 is essentially for the fertilizer industry. That of zone 6 is essentially for the oil refining and explosives manufacturing industries of California, although some of the weak acid is used for fertilizers. These features will be shown in more detail later, as the uses of the sulphuric acid are discussed.

The capacities in these several zones in November, 1918, are given below:

Sulphuric acid manufacturing capacities.

Zone.	Total capacity.		Percentage of total acid capacity.
	Tons per month, expressed as 100 per cent H_2SO_4 .	Tons per year, expressed as 50° B. acid.	
1.....	191,000	3,665,000	38.0
2.....	85,300	1,630,000	17.4
3.....	65,200	1,260,000	13.0
4.....	111,000	2,190,000	22.6
5.....	23,350	448,000	4.6
6.....	22,150	425,000	4.4
Total.....	501,000	9,618,000	100.0

The contact acid capacity was distributed as follows:

Capacities of contact acid plants.

Zone.	Capacity, tons per month, as 100 per cent H_2SO_4 .	Percentage of total contact capacity.
1.....	82,440	41.2
2.....	36,700	18.3
3.....	27,100	13.5
4.....	30,000	15.0
5.....	5,300	2.6
6.....	18,850	9.4
Total.....	200,390	100.0

The chamber capacity was distributed as follows:

Capacity of chamber plants.

Zone.	Tons per month, expressed as 50° B. acid.	Percentage of total.
1.....	175,000	36.4
2.....	77,200	16.0
3.....	61,000	12.6
4.....	134,500	27.9
5.....	28,800	6.0
6.....	5,300	1.1
Total.....	481,800	100.0

The total capacity was divided between (1) Government plants, (2) plants owned by munitions explosives companies, and (3) commercial, fertilizer, and by-product acid plants in the second zone, as follows:

Acid-manufacturing capacity by types of ownership.

(Tons per month expressed as 100 per cent H_2SO_4 .)

Zone.	At government plants.	At explosives companies plants.	At commercial-acid manufacturers' plants.
1.....	3,800	40,800	146,400
2.....	21,200		64,200
3.....		9,200	56,000
4.....	30,000		84,000
5.....		650	22,600
6.....		7,350	14,800
Total.....	55,000	58,630	338,000

The actual production of acid during the year 1918 was 4,650,000 tons on the basis 100 per cent H_2SO_4 , or 7,450,000 tons on the basis 50° B. In October the rate of production had increased to 430,000 tons per month (basis 100 per cent H_2SO_4), or 8,250,000 tons per year (basis 50° B.). The production of high-strength acid—that is, 66° acid or higher—was 2,430,000 tons (basis 100 per cent H_2SO_4). In October the rate of production was 230,000 tons per month, or 2,760,000 tons per year (basis 100 per cent H_2SO_4). During 1918 the average rate of production of the plants was not greater than 90 per cent of the rated capacities, although many plants were actually operating at above their rated capacities. Adverse fuel, labor, and transportation conditions during the greater part of the year tended to reduce production at many plants in the East and North.

LIST OF PLANTS.

The plants in the different zones are listed in the following table:

List of sulphuric acid plants in United States, Jan. 1, 1919.

DISTRICT 1.

Company.	Locality of plant.		Character of plant.
	Town.	State.	
Naugatuck Chemical Co.....	Naugatuck.....	Connecticut.....	Chamber.
Franklin Kaibfeisch Corporation.....	Waterbury.....	do.....	Do.
General Chemical Co.....	Claymont.....	Delaware.....	Contact.
American Agricultural Chemical Co.....	Baltimore.....	Maryland.....	Chamber (3 plants).
Baugh Chemical Co.....	do.....	do.....	Chamber.
Standard Acid Works.....	do.....	do.....	Do.
F. S. Royster Guano Co.....	do.....	do.....	Do.
Virginia-Carolina Chemical Co.....	do.....	do.....	Do.

List of sulphuric acid plants in United States, Jan. 1, 1919—Continued.

Company.	Locality of plant.		Character of plant.
	Town.	State.	
Griffith-Boyd Co.	Baltimore	Maryland	Chamber.
Davison Chemical Co.	do.	do.	Do.
Scott Fertilizer Co.	Elkton	do.	Do.
Naval Proving Grounds	Indianhead	do.	Contact.
Lancaster Chemical Co.	Perryville	do.	Chamber.
Lowell Fertilizer Co.	Boston	Massachusetts	Do.
Merrimac Chemical Co.	Everett	do.	Chamber and contact
Butterworth Judson Corporation	Medford	do.	Chamber.
American Agricultural Chemical Co.	North Weymouth	do.	Do.
Avery Chemical Co.	Tewksbury	do.	Do.
Merrimac Chemical Co.	Woburn	do.	Chamber and contact.
General Chemical Co.	Bayonne	New Jersey	Contact.
Standard Oil Co.	do.	do.	Chamber and contact.
Calco Chemical Co.	Boundbrook	do.	Contact.
King Chemical Co.	do.	do.	Chamber.
General Chemical Co.	Camden	do.	Contact.
American Agricultural Chemical Co.	Carters	do.	Chamber.
Do.	Chrome	do.	Do.
Armour Fertilizer Works	do.	do.	Do.
Franklin Kalbfleisch Corporation	Elizabeth	do.	Do.
American Agricultural Chemical Co.	Elizabethport	do.	Do.
General Chemical Co.	Edgewater	do.	Do.
E. I. du Pont de Nemours & Co.	Deepwater Point	do.	Do.
Do.	Gibbstown	do.	Do.
Grasselli Chemical Co.	Grasselli	do.	Chamber and contact
Mutual Chemical Co.	Jersey City	do.	Chamber.
Hercules Powder Co.	Kenville	do.	Contact.
American Smelting & Refining Co.	Maurer	do.	Chamber.
Butterworth Judson Corporation	Newark	do.	Do.
Do.	do.	do.	Contact.
Harrison Bros. (Inc.)	do.	do.	Do.
Do.	Faulsboro	do.	Do.
E. I. du Pont de Nemours & Co.	Pennsgrove	do.	Contact.
American Cyanamid Co.	Warners	do.	Chamber.
Atlas Powder Co.	Hopatcong	do.	Contact.
Franklin Kalbfleisch Corporation	Brooklyn	New York	Chamber.
Robinson Bros.	do.	do.	Do.
General Chemical Co.	Laurel Hill	do.	Contact.
Trojan Chemical Co.	Allentown	Pennsylvania	Chamber.
Chas. Lennig & Co.	Bridesburg	do.	Do.
Harrison Bros.	Philadelphia	do.	Do.
Do.	do.	do.	Contact.
I. P. Thomas & Sons	do.	do.	Chamber.
Pennsylvania Salt Manufacturing Co.	do.	do.	Do.
Powers-Weighten-Rosengarten Co.	do.	do.	Do.
United Gas Improvement Co.	Point Breeze	do.	Do.
New Jersey Zinc Co.	Palmerton	do.	Contact.
Atlas Powder Co.	Tamaqua	do.	Do.
York Chemical Co.	York	do.	Chamber.
American Agricultural Chemical Co.	Alexandria	Virginia	Do.
E. I. du Pont de Nemours & Co.	Hopewell	do.	Contact.
Virginia-Carolina Chemical Co.	Lynchburg	do.	Chamber.
Robertson Fertilizer Co.	Norfolk	do.	Do.
F. S. Royster Guano Co.	do.	do.	Do.
General Chemical Co.	Pulaski	do.	Contact.
Virginia-Carolina Chemical Co.	Pinners Point	do.	Chamber.
Do.	Richmond	do.	Do.
Do.	do.	do.	Do.
Richmond Guano Co.	do.	do.	Do.

DISTRICT 2.

American Agricultural Chemical Co.	Buffalo	New York	Chamber.
Contact Process Co.	do.	do.	Chamber and contact.
General Chemical Co.	do.	do.	Contact.
Titanium-Alloy Manufacturing Co.	Niagara Falls	do.	Do.
Eastman Kodak Co.	Rochester	do.	Do.
Grasselli Chemical Co.	Canton	Ohio	Chamber.
Do.	Cleveland	do.	Do.

List of sulphuric acid plants in United States, Jan. 1, 1919—Continued.

Company.	Locality of plant.		Character of plant.
	Town.	State.	
General Chemical Co.....	Cleveland.....	Ohio.....	Contact.
American Agricultural Chemical Co.....	do.....	do.....	Chamber.
Do.....	Cincinnati.....	do.....	Do.
Jarecki Chemical Co.....	do.....	do.....	Do.
Virginia-Carolina Chemical Co.....	do.....	do.....	Do.
Farmers' Fertilizer Co.....	Columbus.....	do.....	Do.
Smith Agricultural Chemical Co.....	do.....	do.....	Do.
Grasselli Chemical Co.....	Lockland.....	do.....	Do.
Do.....	Niles.....	do.....	Do.
New Jersey Zinc Co.....	Tiltonville.....	do.....	Contact.
St. Bernard Acid Works.....	St. Bernard.....	do.....	Chamber.
Virginia-Carolina Chemical Co.....	Sandusky.....	do.....	Do.
American Alkali & Acid Co.....	Bradford.....	Pennsylvania.....	Do.
Grasselli Chemical Co.....	Beaver Falls.....	do.....	Do.
American Steel & Wire Co.....	Donora.....	do.....	Do.
F. H. Kahlisch Corporation.....	Erie.....	do.....	Do.
American Zinc & Chemical Co.....	Langeloth.....	do.....	Do.
Pennsylvania Salt Manufacturing Co.....	Natrona.....	do.....	Chamber and contact.
Grasselli Chemical Co.....	Newcastle.....	do.....	Chamber.
General Chemical Co.....	Newell.....	do.....	Contact.
American Sheet Tin & Plate Co.....	Vandergrift.....	do.....	Chamber.
Riverside Acid Works.....	Warren.....	do.....	Do.
Fairmount Chemical Co.....	Fairmount.....	Virginia.....	Do.
United Zinc Smelting Corporation.....	Moundsville.....	West Virginia.....	Do.
United States Government Smokeless Powder Plant.....	Nitro.....	do.....	Contact.

DISTRICT 3.

Hegeler Zinc Co.....	Danville.....	Illinois.....	Chamber.
New Jersey Zinc Co.....	Depue.....	do.....	Contact.
Victor Chemical Co.....	Chicago Heights.....	do.....	Chamber.
Commercial Acid Co.....	East St. Louis.....	do.....	Do.
Do.....	do.....	do.....	Contact.
American Zinc, Lead & Smelting Co.....	do.....	do.....	Chamber.
Do.....	Hillsboro.....	do.....	Do.
Robert Lanyon Zinc & Acid Co.....	do.....	do.....	Do.
Matthiessen & Hegeler Zinc Co.....	LaSalle.....	do.....	Do.
Illinois Zinc Co.....	Peru.....	do.....	Do.
General Chemical Co.....	South Chicago.....	do.....	Contact.
Central Chemical Co.....	West Hammond.....	do.....	Chamber.
Grasselli Chemical Co.....	Grasselli.....	Indiana.....	Do.
Do.....	do.....	do.....	Contact.
E. Rauh & Sons Fertilizer Co.....	Indianapolis.....	do.....	Chamber.
Detroit Chemical Co.....	Detroit.....	Michigan.....	Do.
Cleveland Cliffs Iron Co.....	Marquette.....	do.....	Do.
Atlas Powder Co.....	Atlas.....	Missouri.....	Contact.
New Jersey Zinc Co.....	Mineral Point.....	Wisconsin.....	Do.
E. I. duPont de Nemours & Co.....	Barksdale.....	do.....	Do.
Vinegar Hill Mining Co.....	Platteville.....	do.....	Do.
Wisconsin Zinc Co.....	New Diggings.....	do.....	Do.

^a Not completed.

DISTRICT 4.

Jefferson Fertilizer Co.....	Bessemer.....	Alabama.....	Chamber.
Grasselli Chemical Co.....	Birmingham.....	do.....	Do.
Virginia-Carolina Chemical Co.....	do.....	do.....	Do.
Do.....	Dothan.....	do.....	Do.
Home Guano Co.....	do.....	do.....	Do.
Virginia-Carolina Chemical Co.....	Mobile.....	do.....	Do.
Alabama Chemical Co.....	Montgomery.....	do.....	Do.
American Agricultural Chemical Co.....	do.....	do.....	Do.
Virginia-Carolina Chemical Co.....	Opelika.....	do.....	Do.
Roanoke Guano Co.....	Roanoke.....	do.....	Do.
Virginia-Carolina Chemical Co.....	Selma.....	do.....	Do.
Planters' Chemical & Oil Co.....	Talladega.....	do.....	Do.
Standard Chemical & Oil Co.....	Troy.....	do.....	Do.

List of sulphuric acid plants in United States, Jan. 1, 1919—Continued.

Company.	Locality of plant.		Character of plant.
	Town.	State.	
Southern Sulphur Oil Co.....	Albany.....	Georgia.....	Chamber.
Empire State Chemical Co.....	Arrens.....	do.....	Do.
Armour Fertilizer Co.....	Atlanta.....	do.....	Do.
Morris Fertilizer Co.....	do.....	do.....	Do.
Swift Fertilizer Co.....	do.....	do.....	Do.
Virginia-Carolina Chemical Co.....	do.....	do.....	Do.
Do.....	Augusta.....	do.....	Do.
Southern States Phosphate & Fertilizer Co.....	do.....	do.....	Do.
Black-shear Manufacturing Co.....	Black-shear.....	do.....	Do.
Mandeville Mills.....	Carrollton.....	do.....	Do.
Home Mixture Guano Co.....	Columbus.....	do.....	Do.
Southern Sulphur Ore Co.....	do.....	do.....	Do.
Virginia-Carolina Chemical Co.....	do.....	do.....	Do.
Furman Farm Improvement Co.....	East Point.....	do.....	Do.
Troup Co.....	Lagrange.....	do.....	Do.
Cotton States Feed & Fertilizer Co.....	Macon.....	do.....	Do.
F. S. Royster Guano Co.....	do.....	do.....	Do.
McCabe Chemical Co.....	do.....	do.....	Do.
Virginia-Carolina Chemical Co.....	do.....	do.....	Do.
Do.....	Rome.....	do.....	Do.
Pelham Phosphate Co.....	Pelham.....	do.....	Do.
American Agricultural Chemical Co.....	Savannah.....	do.....	Do.
Mutual Fertilizer Co.....	do.....	do.....	Do.
Phosphate Mining Co.....	do.....	do.....	Do.
The Reliance Fertilizer Co.....	do.....	do.....	Do.
Savannah Guano Co.....	do.....	do.....	Do.
Southern Fertilizer & Chemical Co.....	do.....	do.....	Do.
Virginia-Carolina Chemical Co.....	do.....	do.....	Do.
Georgia Fertilizer & Oil Co.....	Valdosta.....	do.....	Do.
Barker Chemical Co.....	Dunnellton.....	Florida.....	Do.
Armour Fertilizer Works.....	Jacksonville.....	do.....	Do.
Wilson & Toomer Fertilizer Co.....	do.....	do.....	Do.
American Agricultural Chemical Co.....	Pensacola.....	do.....	Do.
E. O. Painter Fertilizer Co.....	Jacksonville.....	do.....	Do.
Union Seed & Fertilizer Co.....	Gretna.....	Louisiana.....	Do.
Planters Fertilizer & Chemical Co.....	New Orleans.....	do.....	Do.
Virginia-Carolina Chemical Co.....	Shreveport.....	do.....	Do.
Swift & Co.....	New Orleans.....	do.....	Do.
Gulfport Fertilizer Co.....	Gulfport.....	Mississippi.....	Do.
Meridian Fertilizer Factory.....	Hattiesburg.....	do.....	Do.
Do.....	Meridian.....	do.....	Do.
Jackson Fertilizer Co.....	Jackson.....	do.....	Do.
Tupelo Fertilizer Co.....	Tupelo.....	do.....	Do.
Acme Manufacturing Co.....	Acme.....	North Carolina.....	Do.
McCabe Chemical Co.....	Charlotte.....	do.....	Do.
Virginia-Carolina Chemical Co.....	do.....	do.....	Do.
Do.....	Durham.....	do.....	Do.
Do.....	Selma.....	do.....	Do.
Do.....	Wadesboro.....	do.....	Do.
Virginia-Carolina Chemical Co. (Almont works).....	Wilmington.....	do.....	Do.
Virginia-Carolina Chemical Co. (Navassa works).....	do.....	do.....	Do.
Virginia-Carolina Chemical Co.....	Winston-Salem.....	do.....	Do.
Caraleigh Phosphate & Fertilizer Works.....	Raleigh.....	do.....	Do.
American Agricultural Chemical Co.....	Wilmington.....	do.....	Do.
Swift Fertilizer Works.....	do.....	do.....	Do.
Anderson Phosphate & Oil Co.....	Anderson.....	South Carolina.....	Do.
Virginia-Carolina Chemical Co.....	Blacksburg.....	do.....	Do.
Do.....	do.....	do.....	Do.
Virginia-Carolina Chemical Co. (Standard works).....	do.....	do.....	Do.
Virginia-Carolina Chemical Co.....	Greenville.....	do.....	Do.
Do.....	Pon Pon.....	do.....	Do.
Virginia-Carolina Chemical Co. (A. C. Stone).....	Charleston.....	do.....	Do.
American Agricultural Chemical Co.....	Columbia.....	do.....	Do.
Do.....	Charleston.....	do.....	Do.
Ettwam Fertilizer Co.....	do.....	do.....	Do.

List of sulphuric acid plants in United States, Jan. 1, 1919—Continued.

Company.	Locality of plant.		Character of plant.
	Town.	State.	
Maybank Fertilizer Co.	Charleston.....	South Carolina....	Chamber.
McCabe Chemical Co.	do.....	do.....	Do.
Planters Fertilizer & Phosphate Co.	do.....	do.....	Do.
Read Phosphate Co.	do.....	do.....	Do.
Royster Guano Co.	Columbia.....	do.....	Do.
Tennessee Copper Co.	Copperhill.....	Tennessee.....	Do.
Ducktown Sulphur, Copper & Iron Co.	Isabella.....	do.....	Do.
Virginia-Carolina Chemical Co.	Memphis.....	do.....	Do.
Armour Fertilizer Works.....	Nashville.....	do.....	Do.
Federal Chemical Co.	do.....	do.....	Do.
Read Phosphate Co.	do.....	do.....	Do.
U. S. Government Smokeless Powder Plant.	do.....	do.....	Contact.

DISTRICT 5.

Commercial Acid Co.	Augusta.....	Arkansas.....	Chamber.
Arkansas Fertilizer Co.	Little Rock.....	do.....	Do.
Ellory Davis Corp. (U. S. Government) ..	do.....	do.....	Do.
Calumet & Arizona Mining Co.	Douglas.....	Arizona.....	Do.
Western Chemical Manufacturing Co.	Denver.....	Colorado.....	Do.
do.....	do.....	do.....	Contact.
E. I. duPont de Nemours Co.	Louviers.....	do.....	Do.
National Zinc Co.	Argentine.....	Kansas.....	Chamber.
Anaconda Copper Mining Co.	Anaconda.....	Montana.....	Do.
E. I. du Pont de Nemours & Co.	Ramsay.....	do.....	Contact.
Mid Continental Chemical Co.	Sand Springs.....	Oklahoma.....	Chamber.
Armour Fertilizer Works.....	Houston.....	Texas.....	Do.
Gulf Refining Co.	Port Arthur.....	do.....	Contact.
Commercial Acid Co.	do.....	do.....	Do.
Sugarland Manufacturing Co.	Sugarland.....	do.....	Chamber.
Hercules Powder Co.	Bacchus.....	Utah.....	Contact.
Garfield Chemical Manufacturing Co.	Garfield.....	do.....	Chamber

DISTRICT 6.

General Chemical Co. of California.....	Bay Point.....	California.....	Contact.
American Agricultural Chemical Co.	Los Angeles.....	do.....	Chamber.
Mountain Copper Co. (Ltd.).....	Martinez.....	do.....	Do.
Barbour Chemical Works.....	Meirose.....	do.....	Do.
Hercules Powder Co.	Pinoie.....	do.....	Contact.
Standard Oil Co. of California.....	Richmond.....	do.....	Do.
Stauffer Chemical Co.	San Francisco.....	do.....	Chamber.
Pacific Guano & Fertilizer Co.	Stege.....	do.....	Do.
E. I. du Pont de Nemours Co.	Du Pont.....	Washington.....	Contact.

CAPACITY OF COMMERCIAL, FERTILIZER, AND BY-PRODUCT PLANTS, JANUARY 1, 1919.

Within a short period after the signing of the armistice the Government plants and many of the munitions explosives companies' plants—that is, plants making acid solely for war munitions—stopped work. All of the commercial and by-product plants that had been using brimstone to supplement their production from pyrite or zinc ores ceased doing so and returned to the normal methods of operation.

If the Government plants be eliminated and those plants built by explosives companies between 1915 and 1918, which will not continue to be operated, the situation as regards potential capacity on January 1, 1919, was about as follows:

Capacity of commercial fertilizer and by-product plants, January 1, 1919.

[Tons per month.]

Zone.	Chamber plants (as 50° B.).	Contact plants (as 100 per cent H_2SO_4).	Total (as 100 per cent H_2SO_4).
1.....	164,000	44,800	147,300
2.....	77,000	15,300	63,400
3.....	61,000	19,000	57,100
4.....	134,000		83,700
5.....	29,000	4,700	22,800
6.....	5,000	11,000	14,100
Total.....	470,000	94,800	388,400

USES OF SULPHURIC ACID.

Sulphuric acid is used in the chemical and metallurgical industries of this country in so many ways that the compilation of a complete list of its uses would be a difficult task. Therefore, only the more important uses are given in the following résumé:

1. Dilute acid—that is, 60° B. (78 per cent H_2SO_4) acid, or weaker—is used in the manufacture of superphosphates, ammonium sulphate, and sulphates of metals (magnesium, aluminum, iron, zinc, copper); in precipitating barium and calcium sulphate for chemical purposes; in the manufacture of mineral acids (nitric, hydrochloric, boric, carbonic, and chromic) and various organic acids (oxalic, tartaric, citric, acetic, and stearic); in pickling sheet iron for tinning and galvanizing; in various metallurgical operations; in the production of copper, zinc, nickel, silver, and gold; for various types of galvanic batteries, storage batteries, electroplating; in the manufacture of ether; in making and purifying many organic coloring matters; in making starch, sirup, and sugar; and in innumerable other chemical and industrial operations.

2. Concentrated acid—that is, acid 60° B. (78 per cent H_2SO_4) to 100 per cent H_2SO_4 —is used for purifying benzene, petroleum, paraffin oil, and other mineral oils; for manufacture of nitroglycerin, pyroxylin, nitrobenzene, picric acid, and various other nitric compounds and nitro ethers; and in the manufacture of the fatty acids by distillation.

3. Fuming acid (oleum) is used principally for the manufacture of various forms of explosives, as nitrocellulose, trinitrotoluol, picric

acid, nitroglycerin; manufacture of certain organo sulphuric acids; and for fortifying weaker acids.

Of all the uses, the following take the greatest tonnage of acid: (1) Manufacture of phosphate fertilizer; (2) refining of petroleum products; (3) pickling of iron and steel; (4) manufacture of nitro-cellulose, nitroglycerin, celluloid, etc.; (5) general chemical and metallurgical operations.

DISTRIBUTION OF ACID IN THE INDUSTRIES.

During June, July, and August, 1918, a comprehensive study of the uses of sulphuric acid in the various industries was undertaken by the Bureau of Mines. Data on the contracts of the acid manufacturers with the consumers, shipments to consumers, and the amounts used for various purposes by the manufacturers themselves during that period were obtained. With this information, covering the consumption of the 390,000 tons of acid (basis 100 per cent H_2SO_4), and the average consumption per month during these months, the data shown in Table 1 were tabulated. The table gives the distribution of acid to various uses for the whole country during the period June to August, 1918.

TABLE 1.—*Distribution of sulphuric acid in the industries, summer of 1918.*

Industry.	Acid used, tons per month (reduced to basis of 100 per cent H_2SO_4).	Tons per year (reduced to 50° B. basis).	Percentage of total acid used.
1. Explosives (military and domestic).....	140,000	2,700,000	36.0
2. Fertilizers.....	111,000	2,130,000	28.4
3. Oil refineries.....	35,000	671,000	8.8
4. Chemicals, drugs, and ammonium sulphate.....	38,500	740,000	9.9
5. Steel pickling and galvanizing.....	36,500	700,000	9.3
6. Fabrics, textiles, etc.....	5,200	100,000	1.3
7. Paints, lithopone, glue, etc.....	5,300	104,000	1.4
8. Metallurgical, including storage batteries.....	15,200	292,000	3.9
9. Miscellaneous.....	3,800	73,000	1.0
Total.....	390,500	7,510,000	100.0

This table shows, eliminating the acid used for munitions and explosives, and allowing about 10,000 tons per month for domestic explosives, an indicated requirement for normal peace industries of possibly 260,000 tons per month (basis, 100 per cent H_2SO_4), or about 5,000,000 tons per year (basis, 50° B.).

Prior to the war the consumption of acid for phosphate fertilizer was about 2,300,000 tons (basis, 50° B.). Up to June, 1919, the consumption of acid for phosphate fertilizers has been more than 2,500,000 tons, or more than 50 per cent of the total production, and

the consumption is without doubt going to increase year by year. Not only is the use of phosphate fertilizer still increasing in the South, but it is beginning to be an important factor west of the Mississippi River. The gradual increase in consumption of phosphate fertilizers in the Middle West and western States will bring into existence acid and phosphate-fertilizer plants in connection with the smelters in Montana and Utah, where much waste gas is available.

The smelters in Montana and Utah should be in position to make phosphate fertilizer for the western markets—that is, west of the Mississippi River and north of St. Louis. In southeastern Idaho, northeastern Utah, and southwestern Wyoming there is plenty of high-grade phosphate rock which can be mined at a comparatively low cost. The freight rate on acid phosphate rock or phosphate fertilizer to the district in question should be no greater from Montana or Utah than from possible southern or eastern producing points, so that no freight-rate handicap will exist. As a matter of fact, freight rates will be such a large item in the cost of the phosphate fertilizer in this district that it will probably be desirable to manufacture and ship into this district a high-grade material that can be diluted again at the point of consumption if necessary. One of the western smelters is now planning to enter this district with a high-grade product, and it is believed that such an industry will ultimately grow to enormous proportions.

The acid being used for fertilizers is nearly all chamber acid. In the South at most plants the plant for acidulating the phosphate rock is in close proximity to or is a part of the acid plant, and little transportation of acid is involved, the acid being pumped directly from the chambers or storage tank to the acidulating tank. When acid is shipped to the fertilizer plant it is usually shipped as 60° B. acid.

Approximately 1 ton of acid (50° B. basis) is required to treat 1 ton of phosphate rock to produce the ordinary superphosphate.

The acid used for refining petroleum is practically all 66° B. acid. Weaker acid is not satisfactory as it will not enter into the reactions involved in decolorizing and deodorizing of the oils by removal of part of the unsaturated hydrocarbons. In a few instances where weaker acid might possibly be used, so much more of it would be required to obtain the results obtainable with the 66° acid that its use is not economical. In petroleum refining, fuming sulphuric acid is used exceptionally; its principal and practically only use is by certain eastern oil refineries in the preparation of colorless and odorless oil (nujol). When fuming acid is used, sulphonates are obtained, known as "Twitchell's reagent."

The amount of acid used per gallon of refined product varies primarily with the character of the crude oil and also with the re-

fining methods employed. In the manufacture of gasoline, the general consumption varies between 0.04 and 0.15 pound of acid (gravity, 66° B.) per gallon, with an average of perhaps 0.10 pound. For refined oils, such as kerosene and illuminating oils, the consumption is between 0.06 and 0.20 pound of acid per gallon, with an average of about 0.12. In the manufacture of lubricating oils, the consumption varies from 0.08 to 0.80 pound per gallon; the average is difficult to estimate, being perhaps 0.40 pound of acid per gallon of oil.

Approximate average figures for the distribution of the acid consumer by refiners among gasoline, kerosene, and lubricating oils throughout the United States, as estimated by the petroleum division of the Bureau of Mines, are as follows: Gasoline, 35 per cent; kerosene, 25 per cent; and lubricating oils, 40 per cent.

The figures for the large and complete eastern refineries are probably more like the following: Gasoline, 20 per cent; kerosene, 20 per cent; lubricating oils, 60 per cent.

In the manufacture of explosives, sulphuric acid is used for two purposes: (1) For the production of nitric acid or mixed acids used in nitrating the organic bodies—that is, cellulose, toluol, phenol, etc.—and (2) as a rehydrating agent. For nitrating purposes 66° B. acid is usually used, but stronger acids are required for dehydrating purposes. The consumption of acid in domestic commercial explosives is about 1.6 pounds of acid per pound of nitroglycerin contained therein. The estimated consumption in manufacturing domestic explosives is about 7,500 tons of acid per month (basis, 100 per cent H_2SO_4). In the manufacture of military explosives the net consumption of acid varies greatly, according to the efficiency of operation of the plant and the amount of acid recovered. From data obtained during 1918 the average consumption of acid at the explosives plants in this country was as follows:

Consumption of acid at explosives plants.

	Pounds of acid (basis, 100 per cent H_2SO_4) per pound of product.
For manufacturing smokeless powder from cotton linter_____	2.3
for manufacturing T N T from toluol_____	2.2
For manufacturing picric acid from benzol_____	6.5

With the gradual elimination of the beehive coke oven by the substitution of the by-product coke plant, there will be more and more ammonia available for the production of ammonium sulphate fertilizer, and this will require more and more sulphuric acid. This requirement may reach a monthly consumption figure of 15,000 tons of acid (basis, 100 per cent H_2SO_4).

For the pickling of steel for tinning and galvanizing purposes, the consumption is approximately 30,000 to 35,000 tons per month (basis,

100 per cent H_2SO_4) when the production of the plate and galvanized ware is heavy. This acid is usually shipped to the pickling plant as 60° acid.

The consumption of sulphuric acid for metallurgical purposes, in connection with the treatment of copper and zinc ores, has increased greatly in the West during the last few years. Part of the acid is used in the flotation of copper, lead, and zinc minerals from their ores. Also a large amount is used in leaching ores and waste tailings for recovery of the copper or zinc content.

The acid made by the Calumet & Arizona Mining Co. is practically all used for leaching carbonate copper ores at Ajo, Ariz. The Anaconda Copper Mining Co. has been producing acid for leaching mill tailings and for leaching zinc ores, as well as supplying acid for the flotation process. The Garfield Chemical Mfg. Co. has been producing acid for leaching low-grade ores from the Utah Copper Co.

The use of acid in certain of these industries has been greatly curtailed in the last year, but will probably be resumed on a large scale in the future. It is believed that the normal requirement of acid in this country in the future will be not less than 270,000 to 300,000 tons per month (basis, 100 per cent H_2SO_4) or about 5,500,000 tons per year (basis, 50° B.).

Although the majority of the manufacturing trades are dependent on supplies of sulphuric acid, yet in comparatively few trades is the cost of the acid an important factor, because the charge for the acid in relation to the total cost of the manufactured goods is often small or even negligible. This applies especially to the textile trades, to leather, paints, etc. In the manufacture of phosphate fertilizers the cost of the acid is a relatively high proportion of the total cost of production. In order to meet the keen competition in the industrial fields efficient working and low cost of production are essential, but the cost becomes a problem of even greater importance in the manufacture of phosphate fertilizers.

Sulphuric acid is a low-priced commodity, but its transportation over long distances is difficult and expensive. Thus the cost of production of acid, which is discussed later, can not be dissociated from the question of the locality of the acid works, because ultimately the cost of the acid as delivered is the deciding factor. The real importance of the cost of any commodity is the cost to the consumer at the point of consumption and not at the producer's works. Thus, although acid may be produced very cheaply as a by-product at smelters in the West, where the raw material (sulphur gases) may be obtained at little or no cost to the acid plant, yet because of the great distance to points of consumption this by-product acid can not compete in eastern markets with acid manufacturers in the East, even though the eastern plants must use expensive raw material.

An acid plant illy situated as to markets or with a capacity much greater than is required for the demand within a comparatively small radius can rarely overcome its haulage handicap by efficient operation. Prior to the war little acid was hauled far in the eastern part of this country. A 200-mile haul for a regular contract delivery of acid over a long period of time was exceptional, for it usually paid the acid manufacturer to build a plant closer to the point of consumption, assuming, of course, the tonnage involved warranted the erection of a plant. During the war this condition was greatly disturbed, especially as regard the haulage of high-strength acid. In the period of exceptionally high prices acid was even shipped from the Pacific coast to New York, from Colorado to Pittsburgh and other points in Pennsylvania, and from the South to the North. With a resumption of normal business conditions, however, such hauls could not continue. Acid is now hauled comparatively short distances, and with the higher freight rates now involved the tendency toward shorter hauls will be even stronger than it has been in the past.

RAW MATERIALS USED IN MANUFACTURE OF SULPHURIC ACID.

TYPES OF MATERIALS USED.

The sulphur-bearing raw materials from which sulphuric acid is made in this country are as follows:

- (1) Brimstone.
- (2) Pyrite ores:
 - (a) Spanish pyrite—cupreous and noncupreous.
 - (b) Domestic pyrite,
 - (c) Canadian pyrite,
 - (d) Pyrite from coal waste.
- (3) Pyrrhotite.
- (4) Zinc ores—crude ores and concentrates.
- (5) Waste sulphur dioxide gases from copper smelting.
- (6) Spent oxide from gas works.

GENERAL DISCUSSION OF MATERIALS USED.

During the early years of the sulphuric acid industry, brimstone was practically the only sulphur-bearing raw material used. In 1882, 85 per cent of the acid produced in this country was made from brimstone, and in 1895 about 75 per cent. From that time on pyrite began to be used more and more, resulting, by 1900, in the almost complete elimination of brimstone for acid manufacture, except in special cases. The production of acid as a by-product in the smelting of zinc ores began in 1895, at a plant at La Salle, Ill., and the

practice has become almost general in the last 20 years at the zinc plants in the Illinois field. In 1907 the practice of manufacturing acid from the waste gases of a copper-blast furnace was inaugurated. The use of pyrrhotite was first successfully demonstrated only about 12 years ago.

In 1914 the acid production of the country was obtained from the following sources, in approximately the following amounts:

Amounts of acid produced in United States from different sources, 1914.

	Tons of 50° B. acid.	Percentage of total.
From brimstone (approximately)-----	100,000	2.6
From pyrite:		
Spanish pyrite-----	1,900,000	50.0
Domestic pyrite, including "coal brasses" and pyrrhotite-----	600,000	15.8
Canadian pyrite-----	300,000	7.9
From roasting zinc ores-----	500,000	13.2
From waste gases at copper smelters-----	400,000	10.5
Total-----	3,800,000	100.0

During the rapid expansion of the acid industry between 1915 and 1918 many of the new plants were built to utilize brimstone alone. In 1917 the use of brimstone was still further augmented by the partial curtailment of the importation of Spanish pyrite, brimstone being substituted for pyrite at many plants. Also many plants burned some brimstone to supplement production from sulphur-bearing ores, especially plants making acid from zinc ores.

In 1917 the acid was produced from the following raw materials, approximately as below:

Amounts of acid produced in United States from different sources, 1917.

	Tons of 50° B. acid.	Percentage of total.
From brimstone-----	2,350,000	32.6
From pyrite:		
Spanish-----	1,650,000	22.9
Domestic, including "coal brasses" and pyrrhotite-----	850,000	11.8
Canadian-----	500,000	6.9
From roasting zinc ore-----	1,300,000	18.1
From waste gases at copper smelters-----	550,000	7.7
Total-----	7,200,000	100.0

In 1918, the further curtailment of the Spanish imports necessitated an even greater substitution of brimstone at plants which formerly had been burning pyrite, as shown in the following table.

The acid production in 1918 was obtained, approximately, as follows:

Amounts of acid produced in United States from different sources, 1918.

	Tons of 50° B. acid.	Percentage of total.
From brimstone-----	3, 580, 000	48. 0
From pyrite:		
Spanish pyrite-----	570, 000	7. 6
Domestic pyrite, including "coal brasses" and pyrrhotite-----	950, 000	12. 7
Canadian pyrite-----	550, 000	7. 5
From roasting zinc ores-----	1, 200, 000	16. 1
From waste gases at copper smelters-----	600, 000	8. 1
Total-----	7, 450, 000	100. 0

With the end of the war, the use of brimstone to supplement other material ceased almost immediately. Several brimstone-burning plants were shut down completely, and at all plants manufacturers began to curtail production. During the spring of 1919 brimstone stocks at acid plants were being gradually used up, and acid manufacturers were inclined not to replenish their stocks until it was apparent that brimstone could be purchased on a parity basis with pyrite ores, the importation of which was gradually resumed.

Whether or not brimstone is largely retained by the acid industry as the raw material of the future or whether there will be a general resumption of the use of pyrite, will depend, of course, upon the relative price of the two kinds of material.

During the war it was necessary at one time to endeavor to establish figures for the relative values to the consumers of sulphur per unit as brimstone or pyrite for the purpose of acid making.

Allowing for the cost of handling each material, the disposal of the cinder from the pyrite, the cleanliness of the gases from the brimstone burners, as compared with the gases from pyrite burners, and all other factors which would affect the cost of manufacture, it was estimated that as a rule if the consumer of pyrite received nothing for the cinder, the brimstone was worth about 3 to 4 cents per unit (a unit equals 1 per cent or 1 unit in a long ton equals 22.4 pounds) more, for acid manufacturing purposes, than sulphur in pure pyrite carrying 40 to 43 per cent sulphur. At certain plants where especially favorable facilities were installed for handling pyrite, the differential would be slightly less. At other plants, especially plants equipped for handling lump material, the differential might be somewhat greater. If copper was present in amounts which made its recovery advisable, this must also be considered. If there was a mar-

ket for the cinder as iron ore, this factor, too, must be taken into consideration.

The following illustration shows the comparison in the cost of burning 10 tons of sulphur per day from 45 per cent pyrite fines and from brimstone. The pyrite is assumed to cost 15 cents per unit, or \$6.75 per ton, and the brimstone to cost 18.5 cents per unit, or \$18.50 per ton, both delivered at the acid plant. The amount of pyrite required per 10 tons of sulphur available is 23.3 tons. The costs for roasting and depreciation are average figures taken from the actual operating data for a number of plants in 1917:

Costs of burning 10 tons of sulphur from pyrite and from brimstone.

	Cost from burning pyrite.
Material, 23.3 tons, at \$6.75 per ton-----	\$157. 25
Handling and roasting ore, 23.3 tons, at \$1.10 per ton-----	25. 65
Handling cinder, 17.5 tons, at 25 cents per ton-----	4. 37
Repairs to and depreciation of burner plant (10 per cent) -	6. 00
Total -----	193. 27
	Cost from burning brimstone.
Material, 10.1 tons, at \$18.50 per ton-----	\$187. 00
Handling and burning, at 60 cents per ton-----	6. 00
Repairs to and depreciation of burner plant (10 per cent) -	1. 00
Total -----	194. 06

If the pyrite and brimstone were purchased f. o. b. the shipper's point, and freight charges are thereby involved, there would be an even greater differential than that indicated.

In the preceding example, if the consumer could obtain \$1.50 per ton for the cinder, he could afford to pay 17.5 cents per unit for the pyrite as against 18½ cents per unit for the brimstone.

These figures in this example are given as an average illustration. The exact differential applicable to any plant will depend on the conditions at the acid plant. At some plants where the roasting equipment has already been amortized, the differential will be less than that given. With an ore containing only 40 or 35 per cent sulphur, the differential will be even greater.

The sources of supply and the character of each of the several types of sulphur-bearing material is discussed in the following paragraphs:

BRIMSTONE.

Native sulphur or brimstone occurs in many parts of the world, generally either in beds of gypsum and associated rocks, or in the region of active and extinct volcanoes. Deposits of sulphur are found in two places in Sicily, and at several places on the mainland of Italy, in considerable quantities. Sulphur is also found in Japan,

Iceland, Mexico, in the Chilean Andes, South America, China, India, and the Philippine Islands. In this country volcanic sulphur is found in the vicinity of numerous hot springs in Wyoming, Idaho, Utah, Nevada, and California. The principal sources of sulphur in this country are the large deposits of natural sulphur, associated with beds of gypsum, in the coastal plains of the Gulf of Mexico.

SICILIAN BRIMSTONE.

Until the year 1903 the greater part of the world's supply of brimstone was mined and prepared for use in Sicily and Italy, about 85 per cent being obtained from Sicily; Japan produced a very small amount. Until the introduction of Louisiana sulphur, extracted by the Frasch process, Sicily controlled the sulphur industry of the world.

The Sicilian mines are distributed over an area of about 100 miles by about 55 miles. The deposits vary in depth from 150 to 650 feet. The brimstone varies considerably in its total sulphur content, from as low as 8 per cent S up to 30 per cent S. Marl, shale, and gypsum are the prominent constituents of the sedimentary rocks in which the sulphur is produced. The sulphur is separated from the associated minerals by fusion and liquation, the heat necessary for the conduct of the process being supplied by the burning of part of the sulphur. With the use of the Gill regenerative furnace,^a the recovery of the sulphur is about 80 per cent, whereas in the old process, where the burning and liquation was carried out in heaps, the recovery was about 60 per cent. This first liquated sulphur, containing 2 to 5 per cent of impurities, is put on the market for acid manufacture in dirty, yellow lumps of irregular shape and size. Refined sulphur is obtained by distillation of the crude material.

During the early years of the sulphuric acid industry in the United States Sicilian brimstone was practically the only sulphur-bearing raw material used. In 1882 only two plants were using pyrite, the rest burning brimstone. The consumption of brimstone in the United States in 1882 was nearly 100,000 tons, about 90 per cent of which was used for acid manufacture.

In 1895^a the consumption of Sicilian brimstone in the United States was about 165,000 tons, of which about 90,000 tons were used for acid manufacture.

In 1900^b the importation of Sicilian sulphur was about 168,000 tons, but only about 50 per cent of this was used for acid manufacture. In 1905^b the Sicilian importation had decreased to less than 75,000 tons, and in 1910^a less than 5,000 tons. The chief reason for

^a Thorpe, T. E., Dictionary of applied chemistry: Sulphur. Vol. 5, 1913, p. 286-312.

^b Figures are from annual volumes of "Mineral Industry," for the years mentioned.

the drop in importation between 1890 and 1895 was because the acid manufacturers in this country were rapidly adopting the use of pyrite in place of brimstone. One of the main causes for the use of pyrite in the place of brimstone for sulphuric acid manufacture during the period around 1895 was the advance in the price of sulphur from about \$15 per ton in New York to about \$25 per ton. This advance was brought about through an agreement made between the Anglo-Sicilian Sulphur Co. and the mine owners, by which the sulphur company controlled at least 75 per cent of the total production of sulphur in Sicily, the company then raising the price. Although the requirements of brimstone for acid manufacture were decreasing from 1900 on, the requirement for brimstone for the paper-pulp and other chemical industries were constantly increasing. However, in 1904 and 1905 the mining of sulphur from the Louisiana deposits by the successful application of the Frasch process resulted in the American product largely supplying the American market to the exclusion of the Sicilian material. All the brimstone requirements of the United States since that time have been met almost entirely by domestic sulphur, with the exception of about 30,000 tons per year on the Pacific coast, which is supplied by Japan, and which is used principally in the paper-pulp industry of the Northwest.

The consumption of brimstone sulphur in this country increased steadily in the period 1900 to 1915, but the increase was due to the growth of the paper-pulp and other chemical industries and not to an extension of the use of brimstone in the sulphuric acid industry. In the period 1910 to 1914, the average consumption of brimstone sulphur in this country was about 300,000 long tons, of which less than 35,000 tons was used in the acid industry.

SULPHUR FROM COASTAL PLAINS OF LOUISIANA AND TEXAS.

The sulphur deposits of Louisiana and Texas are geologically associated with the "dome formations," which are a feature of the coastal plains extending through the States of Louisiana and Texas, into the Gulf States of Mexico. The term "dome" refers to the geologic structure, and the formations are not always indicated by surface elevations. In some places they are indicated by mounds varying from 10 to 80 feet in elevation above the level coastal plains. In some of these domes are found petroleum, rock salt, and sulphur. The oil was first exploited, and it was when drilling for oil near Lake Charles, La., that the first sulphur bed was discovered in 1865. Since then extensive deposits of sulphur have been found in several plains in that district. The most easterly discovery is at Belle Isle, St. Marys Parish, La., and the most westerly at Matagorda Bay, Big Hill, Matagorda County, Tex. These two points are about 225 miles apart, in a northeast and southwest line.

At the domes which are now being mined for sulphur the sulphur lies at a depth of between 600 and 1,100 feet. The overburden consists of clays, sands, quicksands, and gravels, and a comparatively small layer of a soft limestone. The average thickness of the sulphur bed is 125 feet. Beneath the sulphur is gypsum, with occasional layers of sulphur.

Between 1868 and 1895, many attempts were made to obtain the sulphur by ordinary shaft mining and by modifications of the shaft method. All of these attempts failed, owing to the difficulty of resisting the lateral pressures upon the shaft walls of the enormous amount of water in the quicksands encountered, and also the difficulty of preventing the inrush of water from the sands into the sulphur bed, when it had been penetrated.

The present successful method of mining the sulphur was worked out by Herman Frasch, during the years 1892 and 1902, at the sulphur deposit situated near the Parish of Calcasieu, La., 80 miles from Port Arthur, Tex., which deposit Frasch and his associates acquired in the name of the Union Sulphur Co.

The Frasch process involves introducing superheated water into the sulphur beds, through a pipe extending through the quicksands, at a temperature at or above the melting point of sulphur, and then raising the molten sulphur through another pipe to the surface by compressed air. The molten sulphur is then conducted into bins where it solidifies. The wells are 10 to 12 inches in diameter, and contain three strings of concentric pipes. In the outer annular space, the hot water at a temperature of about 175° C. is forced down under a pressure of 250 pounds per square inch. In the inner pipes, hot air at a pressure of 400 pounds per square inch is admitted. The hot water leaves the outer pipe at several points slightly above the bottom of the pipe, enters the sulphur-bearing formation, and after the brimstone has been thoroughly heated, additional quantities of water, which is constantly being forced into the formation, melt the sulphur (melting point 115° C.), which sinks toward the bottom of the sulphur bed, to the bottom of the well. Hot compressed air is forced down the inner pipe, which is slightly longer than the others, issues from the bottom of that pipe, and flows up through the intermediate annular space between the air pipe and the second pipe. As the liquid sulphur covers the entrance to that annular space, the sulphur is lifted to the surface by the ascending air. One of the most important features of the process is the maintenance of proper balance between the pressure of the superheated water, and the air pressure, so as to permit an uninterrupted flow of sulphur to the surface. On reaching the surface the sulphur is conducted through a pipe, supported on light framework, to a bin in which it solidifies. There are a series of bins, about 150 feet

by 250 feet by 65 feet high. The sulphur is delivered into the center of these bins, and caused to spread in layers about one inch in thickness.

The method of mining sulphur described above was patented by Frasch in 1891. In 1905, 1910, and 1911 further patents were obtained to cover certain details in the process. With the belief that at the expiration of the Frasch patent, in 1908, the fundamentals of the process became public property under the provisions of the patent laws, the Freeport Sulphur Co. started the operation of a property in Texas, using a modification of the process. The consequence has been recent litigation involving the patents granted in 1905 and 1910 to the Union Sulphur Co. As a result of the litigation, which was carried to the highest courts, the process is now open to all.

Crude oil is used for firing the boilers to supply the necessary heat and power, and the commercial success of the Frasch process is due in a large measure to the local availability and cheapness of the fuel oil. It has been estimated that of the total heat units employed less than 2 per cent are utilized in melting the sulphur. The temperature of the quicksand water, of which there is a great influx to the sulphur bed during the operation of the process, is low and has to be raised before the sulphur can be melted. The well gives out when the cavity from which the sulphur has been extracted becomes too large to permit of the necessary temperature being maintained.

The rocks above the sulphur-bearing beds are not strong enough to support the dome after much sulphur has been extracted. At the property of the Union Sulphur Co., which has been worked steadily since 1895, it has been necessary to employ a dredge constantly to pump material from adjacent areas onto the settled ground in order to hold the level. It is estimated that in places at this property the original surface is 200 feet below the present surface, which at the most is only about 25 feet above sea level.

The development of a sulphur property and the equipment for operation requires large expenditures. Prospecting can only be done satisfactorily by drilling, the number of drill holes necessary to establish the existence of a deposit varying with the nature of the deposit. In recent years it has cost in the neighborhood of \$5,000 per hole for drilling at plants located near good transportation facilities. At the present time it would probably require an investment of one to two million dollars to develop and place in production a property extending over an area of perhaps 300 acres. A large quantity of sulphur must, therefore, first be actually determined to insure the return of the invested capital plus a reasonable profit.

There are now three properties producing sulphur by the use of the Frasch process or a modification of that process: The Union Sulphur Co., at Sulphur, near Lake Charles, La.; the Freeport Sul-

phur Co., at Bryant Heights, Tex.; and the Texas Gulf Sulphur Co., at Matagorda, Tex.

UNION SULPHUR CO.

The Union Sulphur Co. in 1902 began to produce sulphur on a practical scale, and by 1905 the production had increased to over 200,000 long tons per year. From that time the yearly production was usually greater than the requirement, and some stocks were accumulated above ground. By October, 1917, when a special commission of the Bureau of Mines and the United States Geological Survey visited the property, the production had been increased to 2,000 tons per day, which at that time was considered a maximum output with the equipment installed. There were then more than 800,000 long tons of sulphur above ground at the property.

Under the stress of the war-time requirement, and the necessity of maintaining an adequate stock above ground to meet any emergency, the production was further increased during the first six months of 1918, till by June, 1918, the production had reached nearly 4,000 tons per day, and the stock above ground had been increased to about 1,000,000 tons.

The operations of the company were interrupted on August 7, 1918, by a tornado which blew down all the derricks over the wells, all the pipe lines, etc., and also the smokestacks of the boiler plants. Within a few weeks, however, new wells had been drilled and equipped with piping and connected to the boilers and mining resumed. By early October the production was again about 4,000 tons per day, and could have been still further increased.

Brimstone is shipped from Sulphur, La., by rail direct to the points of consumption, or over a special line 68 miles long to Port Sabine, Tex., where it is loaded onto ships. Prior to 1917, about one-fourth of the total shipment was made all rail, and three-fourths by rail to Sabine and then by ships.

For an average daily production of about 2,000 tons, there are required about 4,000 barrels of fuel oil. The labor required for production at this rate is about 800 men. About 8,000,000 gallons of water are pumped and heated each 24 hours.

The sulphur-bearing deposit at this property is only about 64 acres in extent, but is apparently of unusual richness, and it is believed may be depended on for many years to produce sulphur at a reasonable cost. During the war period the mining cost rose to about \$10 per ton, but prior to 1917 was less than \$6 per ton. According to a report of the Federal Trade Commission (S. Doc. No. 248), the cost during the first half of 1917 was \$5.75 per ton.

FREEPORT SULPHUR CO.

The property of the Freeport Sulphur Co. is located at Bryant Heights, about 40 miles from Galveston, and within 3 miles of the

coast. The deposit comprises a number of scattered bodies spread over a large area (about 520 acres), considerably larger than that worked by the Union Sulphur Co. On account of this fact the cost of production at Freeport undoubtedly is a little higher than at the Union property. According to the report of the Federal Trade Commission (S. Doc. 248), the cost during the first six months of 1918 was \$6.15 per ton.

The company began to produce in 1913. During the first nine months of 1917 the production averaged about 1,500 tons per day, which was considered to be the maximum rate of production with the equipment then installed.

In working this property to produce 1,500 tons per day, about 8,000,000 gallons of water are pumped and heated. The boiler capacity of the plant is about 25,000 horsepower.

TEXAS GULF SULPHUR CO.

The property of the Texas Gulf Sulphur Co. is located on the Matagorda Big Hill, in Matagorda County, Tex., within one-half mile of Matagorda Bay and about 6 miles from the deep water of the Gulf. The property is reached by a branch of the Atchison, Topeka & Santa Fe Railway from Bay City to Matagorda.

The company's holdings cover 300 to 400 acres, on or adjacent to the mound, which itself covers 200 to 300 acres, and rises about 35 feet above sea level. Matagorda Big Hill is a typical "saline dome." Extending to a depth of 800 to 1,000 feet below the surface is sand, shale, clay, and gravel; below these unconsolidated sediments is a "cap rock" of limestone. The sulphur occurs immediately below the limestone at depths of 870 to 1,215 feet, depending on its location in the dome, and varies in thickness from 60 to 90 feet. A stratum of salt and gypsum is found underneath the sulphur bed. The average sulphur content of the sulphur bed varies from 20 to 40 per cent. It is estimated that there are over 10,000,000 tons of sulphur available in the deposit.

Actual operations were started early in March, 1919. Several wells are now in operation, producing about 1,500 tons a day.^a

OTHER PROPERTIES.

Besides the three properties mentioned, which are now mining sulphur, the following properties on the coastal plain are possible potential producers:

1. The Texas Exploration Co. property, Damon Mound, northwestern Brazoria County, Tex., about 35 miles northwest of Freeport on a branch of the Southern Pacific Railway connecting with the

^a See news item, Operations of the properties of the Texas Gulf Sulphur Co., Eng. and Min. Jour., vol. 107, Mar. 29, 1919, pp. 555-557.

main line at Rosenberg, 18 miles north of Damon Mound. It is claimed that at least 3,000,000 tons of sulphur have been definitely developed by drilling.

2. The Texas Co. property, Haskins Mound, Brazoria County, Tex., 4 miles west from Chocolate Bay and 8 miles northwest from the Gulf Coast.

Many other localities along the coastal plains offer possibilities for developing sulphur deposits, but none of them has been sufficiently prospected to estimate the reserves, or the conditions for mining. Some of the localities which have known possibilities for production are: (1) Hackley, in Harris County, 25 miles northwest of Houston; (2) Liberty, about 3 miles south of Liberty Station on the Southern Pacific Railway; (3) Barbers Hill, 9 miles southeast of Wattey Station; and (4) Hackberry Island, in Cameron Parish, La., 18 miles southwest of Lake Charles, and 12 miles from the Gulf coast. In fact, the Gulf coast district offers promises for the development of several large deposits in the future, as the demand for sulphur increases. It is rather doubtful, however, whether there will be any extensive development of these deposits for years to come. A deposit, to be successfully worked, would have to occur under conditions exceptionally favorable for low cost of production and have easy transportation facilities.

Prior to the extraordinary condition created by the war, the Union Sulphur Co. and the Freeport Sulphur Co. were more than able to care for the brimstone demand in this country. To the production capacity of these two companies is now added that of the third, the Texas Gulf Co. The future requirements for brimstone are rather problematical, as it is not certain to what extent brimstone will continue to be used in acid manufacture in place of pyrite. To compete with pyrite, brimstone will probably have to sell at a price which will not encourage anyone not now in the field to make heavy investments in the development of the "domes."

SULPHUR DEPOSITS IN WEST TEXAS AND OTHER DISTRICTS IN THE WEST.

Within the last 15 years several attempts have been made to mine and extract sulphur from the deposits found in an extensive belt of gypsum in Culberson County, Tex.^a So far these attempts have not been an economical success.

The sulphur occurs in the gypsum and limestone beds either as layers more or less parallel with the stratifications of the rocks,

^a Richardson, G. B., Contributions to economic geology—salt, gypsum, and petroleum in trans-Pecos Texas, U. S. Geol. Survey Bull. 269, 1904, pp. 572-585; Perch. L. C., jr., The Rustler Springs sulphur deposits, Univ. Texas Bull. 1722, April 15, 1917. pp. 57-59.

or as cementing material within the coarsely crystallized gypsum, or as amorphous bunches within the rock.

The relatively most extensive operations with this material have been conducted by the Michigan Sulphur & Oil Co. An attempt was made to extract the sulphur by the White steam process, which consisted of loading sorted ore, containing about 40 per cent sulphur, into perforated sheet-iron cars, and running the cars into a horizontal cylindrical retort, into which steam, at 60-pound pressure, was admitted for $2\frac{1}{2}$ hours. About 60 to 65 per cent of the sulphur contained in the ore was liquated out, but on account of the high cost of fuel the production was unprofitable.

The West Texas Sulphur Co. has erected a plant to treat the ore under a modification of the steaming process described.

The district as a whole appears to have a large quantity of sulphur, apparently scattered through a large number of small deposits. It is problematical whether any one of these could be exploited to advantage by individual efforts, under the present conditions as to market, etc., but the deposits are potential sources of supply for the future.

In 1918 some tests were conducted by J. M. Hyde at the Bureau of Mines experiment station at Berkeley, Calif., to determine the possibility of recovering the sulphur from this ore by flotation. These tests showed that a high recovery, about 80 per cent, could be obtained in a concentrate carrying about 85 per cent sulphur.

Various small sulphur deposits have been located in Colorado, chief among them being the Vulcan mine, near Iola, in Gunnison County, and the property of the Colorado Sulphur Production Co., near Creede, in Mineral County. The Vulcan mine has been operated at intervals for the past 20 years, but so far unsuccessfully. The distillation of the sulphur from this mine has resulted in a product containing selenium, which is detrimental to the use of the sulphur in the manufacture of acid. The property near Creede has not been worked, though an effort was made in 1918 to start operations there.

In Wyoming, deposits of sulphur have been found in various places,^a but the only two properties that have been worked are those near Cody, in Park County, and Thermopolis, in Hot Springs County. The Cody Sulphur Co. and Yellowstone Sulphur Co. have operated intermittently during the last 20 years near Cody, but, primarily because of the difficulties in obtaining an economical re-

^a Woodruff, E. G., Sulphur deposits at Cody, Wyo., U. S. Geol. Survey Bull. 340, 1907, pp. 451-456; Sulphur deposits near Thermopolis, Wyo., U. S. Geol. Survey Bull. 380, 1909, pp. 373-380. Hewett, D. F., Sulphur deposits of Sunlight Basin, Wyo., U. S. Geol. Survey Bull. 520, 1911, pp. 350-362; Sulphur deposits in Park County, Wyo., U. S. Geol. Survey Bull. 590, 1914, pp. 477-480.

covery, the production has been small. Sulphur deposits near Thermopolis have also been worked by various companies, but the production has been small. It is not probable that this Wyoming district will ever become a large and constant producer of sulphur.

In Utah, sulphur has been reported at various places. The only producing property is that of the Utah Sulphur Corporation, located 27 miles from Black Rock on the Salt Lake Railroad, at a mining camp called Morrissey (formerly Sulphurdale). The deposit has been described by Lee.^a The sulphur produced in this property has been sold to the beet-sugar refineries. On account of the high cost of recovery, and the long haul, this sulphur could not be considered available for acid manufacture in the East.

In Idaho a sulphur deposit is being developed by the Idaho Sulphur Co., about five miles east of Soda Springs (on the Oregon Short Line Railroad) in Bannock County. The deposit has been described by Richards and Bridges.^b The commercial possibilities of this project are not yet demonstrated. If the treatment problem is solved successfully this property probably can produce a considerable tonnage for the Pacific coast market.

In California sulphur showings are reported in various districts, but from the information available regarding them it is apparent that they are small and relatively unimportant as far as constituting a possible source of supply to the acid industry of the Pacific coast is concerned.

In Nevada the two producers are the property of the Cuprite Esmeralda Sulphur Co., at Cuprite, Nye County, and the property of the Nevada Sulphur Co., located at Sulphur, Humboldt County.

The western deposits, as a rule, are of uncertain character, and their tonnage yields would be comparatively small. Their general great distance from consuming centers has been detrimental to their development in the past and is likely to remain so in the near future. However, with proper solutions of the treatment problems and improved transportation facilities the aggregate production from these deposits may be made to take care of the western consumption.

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^a Lee, W. T., The Cove Creek sulphur beds, *U. S. Geol. Survey Bull.* 315, 1906, pp. 485-489.

^b Richards, R. W., and Bridges, J. H., Sulphur deposits near Soda Springs, Wyo.: *U. S. Geol. Survey Bull.* 470, 1910, pp. 499-503.

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PYRITE.

GENERAL CONSIDERATIONS REGARDING CHEMICAL CONSTITUENTS.

Pure pyrite contains 53.4 per cent sulphur and 46.6 per cent iron. Pyrite suitable for acid manufacture should contain in general as much sulphur as possible. Under ordinary conditions most of the acid manufacturers require a pyrite containing not less than 42 per cent sulphur. Under extraordinary conditions, such as existed in certain localities during the war, pyrite containing as low as 30 per cent sulphur was used. Pyrite containing less than 30 per cent usually was not used alone, but in conjunction with pyrite higher in sulphur or with brimstone.

The content of available sulphur in general determines the value of the pyrite to the consumer, although the physical characteristics of the ore also are important. With pure ores and with the proper types of roasters and skillful operation it is possible to reduce the sulphur content of the cinder to less than one-half per cent. In practice, however, the sulphur content of the residue is seldom less than 2 per cent. With ores containing impurities, such as zinc, copper, lead, lime, and magnesia, it is practically impossible to reduce the sulphur content to such a low percentage, even with the most skillful manipulation. This is due largely to the formation of sulphate of these metals, which are not decomposed by the temperature of the roasters.

Discussing the question of the effect of these impurities on the availability of the sulphur, Falding^a says:

When ores contain among others of minor importance the following minerals, they will, at the ordinary temperature of burners used by sulphuric acid manu-

^a Falding, F. J., The manufacture of sulphuric acid: Mineral Industry, vol. 7, 1898, p. 653-654.

facturers, retain in chemical combination the following proportion of sulphur, which will, therefore, not be available for making acid:

For each per cent of.....	Cu	Zn	Pb	CaO	MgO
There will be found (per cent S).....	0.50	0.50	0.15	0.57	0.80

This is on the assumption that all the sulphides are converted to sulphates, which is by no means the case.

The amount of sulphur retained by these substances varies according to the roasting condition and to the physical character of the ore, and actual operating experience with any particular ore is necessary to determine the actual sulphur retained by it. For example, during a recent experiment conducted over several months by a large and carefully operated acid plant, in which noncupreous Spanish pyrite was burned in comparison with a domestic copper ore, the latter, in spite of its copper content, yielded a cinder with an average sulphur content 0.4 per cent less than the noncupreous Spanish ore. This result was due to the fact that the physical characteristics of the domestic ore made it much more free burning than the fine textured, noncupreous Spanish ore. With zinc, lead, lime, or magnesia present the retention of sulphur by these impurities would be more nearly as indicated above, regardless of the physical condition of the ore.

In general, the figures in the preceding table give a basis for a settlement in the absence of any data obtained from actual roasting of ore. For example, an ore containing, say, 42 per cent sulphur, and 3 per cent zinc, 2 per cent CaO, and 1 per cent MgO, will have only about 37.6 per cent available sulphur. The impurities will retain 3.4 per cent, and the calcine from even a pure ore will retain the equivalent of at least 1 per cent of the sulphur in the original ore, so that the total unavailable sulphur is about 4.4 per cent, giving 37.6 per cent as available, or about 90 per cent of the total sulphur content.

Pyrite ore is usually sold at a price per unit of sulphur by analysis. If the ore mentioned above is sold at a price of 10 cents per unit the cost of the ore to the consumer is \$4.20 per ton (2,240 pounds). However, as only 90 per cent of the sulphur is available for acid manufacture, the actual cost of the available sulphur per unit is 11-1/9 cents.

With the same proportion of impurities, an ore having a higher sulphur content is of greater value per unit of sulphur than an ore having a lower content. Assume two pyrite ores to be free from the impurities that would retain sulphur, one containing 45 per cent sulphur, and the other, 40 per cent sulphur. It is readily possible that under

suitable roasting conditions the sulphur content of the residues from the two ores may be reduced to 2.0 per cent. However, in order to obtain the same units of available sulphur, it is necessary to roast 1.125 tons of the ore carrying 40 per cent sulphur for every ton of the ore containing 45 per cent sulphur. Thus the cost of freight, loading, unloading, crushing, and roasting per unit of available sulphur is $12\frac{1}{2}$ per cent greater for the 40 per cent ore than for the 45 per cent ore.

As regards the proportional values of sulphur in 45 per cent ore and in 35 per cent ore the difference is still greater, because it is well-nigh impossible to reduce the sulphur content of the cinder as low in burning 35 per cent ore as in burning the 45 per cent ore, without the use of a special type of roaster or of external heat. The cinder from an ore containing originally only 35 per cent sulphur will seldom carry less than $2\frac{1}{2}$ and usually carries 4 per cent sulphur. Thus, in order to obtain the same number of available units of sulphur, it is necessary to handle 37 per cent more of the 35 per cent ore than it would of the 45 per cent ore.

The other constituents of the ore which have a deleterious effect in the manufacturing processes, or which reduce the value of the pyrite for acid manufacture, are arsenic, selenium, and other volatile metallic compounds, including compounds giving off chlorine or fluorine in roasting.

Arsenic and selenium in proportions less than 0.20 per cent are of little or no consequence in the manufacture of acid by the chamber process. In fact, at several chamber plants, ores containing as high as 1.0 per cent are being utilized. However, with a large proportion of arsenic present, the fumes of arsenic trioxide tend to clog the flues and towers, and the acid produced therefrom contains sufficient arsenic to corrode the chambers. Arsenic is very deleterious to the contact process, and when ores containing even a trace of arsenic are used in connection with this process, the arsenic must be completely removed by an elaborate and rather expensive cleaning system. If the ores contain more than 0.2 per cent arsenic the necessary cleaning system would be so elaborate that the cost of removal would be excessive, and ores with that high an arsenic content are not suitable in any way to the contact process.

With the proportions commonly encountered in pyrite ores, these impurities are seldom present in the acid in amounts of any consequence to the fertilizer manufacturer, or to some other manufacturers. In acid intended for "pickling" iron previous to tinning, or to galvanizing, or for the drug trade, or for the general use of the chemical trade, they are inadmissible. In general, ores containing less than 0.1 per cent arsenic are termed nonarsenical and are sold for a higher

price than arsenical ores. The differential in price, as a rule, is between 0.5 and 1.0 cent per unit. As a matter of fact, the penalty for any arsenical ore, especially ore with a high arsenic content, may well be as much as 2 cents per unit in certain localities.

Volatile metallic compounds are deleterious in that they are carried into the flues and tend to clog the Glover towers and to make "dirty" acid—that is, acid containing these metals either in solution or in finely divided suspensions.

Chlorine and fluorine are especially undesirable at contact acid plants, as will be discussed in a subsequent connection.

Fluorine is injurious to the lead chambers, and to the packing in the Glover tower at acid plants. Thus, fluorides are not desirable in pyrite.

Another objectionable impurity in pyrite is coal, from which hydrocarbons may be distilled, carrying off carbon which contaminates the acid. Coal or carbon is objectionable in the raw material for contact plants, as any carbon monoxide which may be formed is a detriment to the contact process.

GENERAL DISCUSSION REGARDING PHYSICAL CONDITION.

Although there have been no widely accepted standards, pyrite has been sold generally in three sizes—lump, "furnace," and fines.

Lump ore contains no pieces over 18 inches in size, and all the fines have been screened out.

"Furnace" ore has been sized through a $2\frac{1}{2}$ -inch or 3-inch screen, or ring, onto a $\frac{1}{4}$ -inch screen. Not more than 5 per cent of the ore should be finer than one-quarter inch.

More careful sizing of "furnace" ore than the above should be employed to get the best results in lump burners. This feature is discussed in connection with the operation of lump burners.

Fine ore includes all ore and concentrate which will pass through a $\frac{1}{4}$ -inch screen.

A large consumer having burners for both lump and fines may buy lump ore or "run-of-mine ore" and crush and screen it to provide the desired proportions of lump and fines. The purchaser is usually allowed 25 to 50 cents per ton to cover the cost of crushing and screening.

In this country heretofore it has been customary to price Spanish ore fines at about 2 cents per unit of sulphur less than the price of furnace size.

Some ores act explosively or decrepitate in the burners. Thus certain furnace-size ores may produce a large amount of fines in the burners, which will fall through the grates unburned, causing high sulphur losses and possibly other detrimental features, such as clinker-

ing and matting on the grate bars. Decrepitation is due generally to the presence of hydrated silicates and can be prevented only by a preliminary heating before burning.

Certain pyrite ores burn more readily than others—that is, are free burning—because of the physical character of the particles of ore, whether granular or in a dense mass of fine-grained particles. Such characteristics can be determined only by test.

PYRITE-BURNING CAPACITY IN UNITED STATES.

The total sulphur requirements in the form of fine and lump pyrite ore, if all pyrite-burning equipment in this country should be operated at capacity on pyrite alone, would amount to 840,000 long tons, of which 480,000 tons would be sulphur in lump ores. This would be equivalent to about 2,500,000 tons of pyrite containing 40 per cent sulphur.

Of the total pyrite requirements almost 50 per cent is for the acid plants in zone 1—that is, along the Atlantic seaboard north of the North Carolina line. The following table gives the approximate requirements of sulphur in the form of lump and fine pyrite in the several zones:

Sulphur required in the form of pyrite to operate all plants in United States equipped with pyrite burners.

Zone.	Fines.		Lump or furnace size.	
	Long tons.	Percent- age of total fines.	Long tons.	Percent- age of total lump.
1.....	290,000	60.4	135,000	37.5
2.....	53,000	10.9	63,000	18.0
3.....	27,000	5.5	19,000	5.2
4.....	57,000	12.0	138,000	37.8
5 and 6.....	53,000	11.2	5,000	1.5
	480,000	100.0	360,000	100.0

SPANISH PYRITE.

The pyrite deposits of southern Spain and Portugal are by far the most important in the world, as before the war they supplied about 70 per cent of the world's consumption of pyrite. The area in which deposits are situated is about 100 miles long by 12 to 18 miles wide and extends from Aznol-Collar, in Spain, to San Domingos, in Portugal. The total resources of ore in this district are estimated, by J. H. L. Vogh, a Norwegian geologist, to be about 1,000,000,000 tons.

The annual production from this area is about 4,000,000 tons, of which 400,000 tons is obtained from Portugal, the rest from Spain.

In 1910 the exports of pyrite from Spain were distributed about as follows:

Exports of pyrite from Spain, 1910.

To—	Long tons.
United States and Canada-----	700,000
Germany -----	800,000
England-----	800,000
France and Belgium-----	500,000

Only the high-grade smelting ores, ores of low sulphur content, and a small amount diverted to the local phosphate industry are retained in the country.

The ores may be classed roughly as follows:

1. Ore containing over 5 per cent copper, smelting grade, retained in Spain.

2. Ore containing $1\frac{1}{2}$ to 5 per cent copper. This ore is largely exported to European points for the recovery of copper, sulphur, and iron.

3. Ore containing about $1\frac{1}{2}$ per cent copper.

4. Ores containing too small a percentage of copper to warrant recovery of the copper. These ores are sold only for the sulphur content.

The deposits are worked by open-cut methods, with a mining cost, including cost of removal of the overburden, of approximately \$1 per ton. The ore is transported 30 miles to Huelva, where it is dumped into ore pockets, from there into vessels. Ore containing 49 per cent sulphur has been sold f. o. b. Huelva for less than \$3 per ton.

A considerable part of the ore of class 3, which is shipped to America, is first treated at the mines by being spread out in beds and exposed to the weather. The beds are turned over or stirred at intervals and are frequently wet down with water to leach out the copper, which has been rendered soluble by the atmospheric oxidation and by the action of ferric sulphate. In about three years' treatment of this kind the copper content is reduced to about 0.3 per cent, the iron pyrite remaining practically unchanged. The sulphur content is frequently increased. The ore is then sold as "washed ore."

Two of the companies selling Spanish pyrite ores in this country dispose of part of the copper-bearing unwashed ores under a form of contract by which the sulphur content alone is paid for, the pyrite cinder reverting to them. These companies have plants for treating the cinder for the recovery of the copper by a chlorination and lixiviation process, after which the residue is sintered and shipped to the iron furnaces.

The chief importers of Spanish pyrite ore in this country have been:

Pyrites Co. (Ltd.); offices in London and New York; leaching and sintering plants at Wilmington, Del., and Roanoke, Va.

Pennsylvania Salt Mfg. Co.; offices in Philadelphia, Pa.; leaching and nodulizing plants at Philadelphia and Natrona, Pa.

Naylor & Co.; offices in New York.

Davis Sulphur Ore Co.; offices in New York.

Ladenburg, Thalman & Co.; offices in New York. This company ships ore from Pomaron, Portugal.

In 1895 and 1905 the New York price for Spanish ore was 10 cents per unit of sulphur. Just before the war the price was 12 to 12½ cents per unit. At that time freight rates from Spanish ports to New York were between \$2.25 and \$2.50 per ton. In the contracts for the sale of Rio Tinto ore prevailing before the war, when the cinder was retained by the buyer, \$1 to \$1.50 per ton of pyrite was charged in addition to the charge for sulphur. This charge was based on the value of the iron content of the ore to the iron industry. The treatment of the pyrite cinder to prepare it for the iron blast furnace, such as briqueting, nodulizing, and sintering, is discussed elsewhere in this report (pp. 204 to 207).

The sulphur content of the Spanish ore imported to this country varies between 45 and 50 per cent—the lump will run 47 to 49 per cent and the fine 45 to 47 per cent. The arsenic content occasionally runs as high as 0.8 per cent, but averages about 0.36 per cent. The lead and zinc contents usually total less than 1 per cent.

Prior to 1890 the importation of Spanish pyrite was less than 20,000 tons. During the period 1890 to 1900 the importations had increased to about 300,000 tons per year. By 1910 the importations had increased to 700,000 tons. In 1914 about 900,000 tons were imported. The greatest tonnage imported in any year was in 1916, when 1,200,000 tons were received, the heavy demand, of course, being due to the large acid requirements for the manufacture of munitions. In 1917 the importation was reduced to about 750,000 tons, this decrease being due to the shortage in ships.

The difficulty of obtaining ships became even greater in the early months of 1918, and the importations in the first three months averaged less than 50,000 tons per month. In April, 1918, it became necessary for the United States Shipping Board to ask for a still greater curtailment in the importations. As a result of a conference held under the auspices of the War Industries Board in April, at which representatives of the importers and the consumers were present, the importations were restricted to a total of 125,000 tons between April 1 and October 1, 1918. The amount of pyrite actually imported during that time, however, was less than the allowable

125,000 tons. The total importations of Spanish ore during the year 1918 was about 270,000 tons.

The principal ports of entry of the Spanish ore for the last five years have been New York, Philadelphia, and Baltimore, between 55 per cent and 60 per cent of the total importation going through these ports. Charleston, S. C., and Savannah, Ga., each receive about 10 per cent, most of the rest being received at Boston, Mass., Norfolk, Va., Wilmington, N. C., Jacksonville, Fla., and New Orleans, La.

During the war the price of Spanish ore was greatly increased over the prewar prices, because of the high freight rates. The ore was sold to the consumer usually on a basis of the old prewar quotations plus the excess freight charges, which brought the price in the South Atlantic ports to as high as 35 cents per unit, with an average of perhaps 30 cents.

Since the first of the year, 1919, the freight rates from Huelva to New York have been decreased to \$3.50 to \$4 per ton. With that rate the Spanish ore was quoted in July in New York at about 16 cents per unit of sulphur.

Spanish ore is sold both in "furnace size" and in fines size, the furnace ore going primarily into the South, where the greater proportion of the plants having lump-burner equipment are situated, and the fines going to the northern acid plants. It has been customary to price the Spanish fines at about 2 cents per unit less than the market price of the furnace size. This is due to the fact that as a rule the Spanish ore is of very fine texture and the fines from the ore contains a great deal of "float dust." This fine dust rising with the gases from the furnace tends to clog the flues, towers, and the entire chamber system, and the fines tend to cake in the hottest part of the furnace. In fact, Spanish fines have given so much difficulty in manipulation that the acid manufacture has penalized the fines to some extent, though as a matter of fact the differential is arbitrary.

DOMESTIC PYRITE.

GROWTH IN PRODUCTION.

Prior to 1885 the production of pyrite in this country was less than 50,000 tons per year. By 1890 the production had been increased to about 100,000 tons per year, and this was about the rate of production till 1895 and 1896. At that time the new acid plants in the South were beginning to require more pyrite, with the result that the production was rapidly raised to about 200,000 tons per year in 1900. About 70 per cent of this production was from Virginia and North Carolina, 25 per cent from Massachusetts and New York, and the rest from California and Colorado. By 1905 the production had increased to about 250,000 tons, and this was approximately the rate up to and including 1910. Of this production, about

48 per cent came from Virginia, 20 per cent from California, 20 per cent from Massachusetts and New York, 7 per cent from Alabama and Georgia, and the rest largely from Illinois and Ohio. Since 1910 the production has been as follows:

Production of pyrite in the United States, 1911-1917.^a

Year.	Tons.	Year.	Tons.
1911.....	299,904	1915.....	394,124
1912.....	350,928	1916.....	423,556
1913.....	341,338	1917.....	462,662
1914.....	336,662	1918.....	464,494

^a From statistics compiled by United States Geological Survey.

In 1913 the total production, about 341,000 tons, was obtained from the States as follows:

Production of pyrite by States, 1913.

From—	Tons.	Per cent.
Virginia.....	148,200	43.5
California.....	70,500	20.6
Wisconsin.....	25,200	7.4
Georgia.....	11,100	3.2
Illinois.....	11,200	3.3
Indiana and Ohio.....	14,800	4.4
Other States.....	60,000	17.6
Total.....	341,000	100.0

In 1918 the total production, about 464,000 tons, was obtained as follows:

Production of pyrite by States, 1918.^a

From—	Tons.	Per cent.
Virginia.....	143,427	30.8
California.....	111,861	23.9
New York.....	63,982	13.7
Georgia.....	31,315	6.7
Illinois.....	24,369	5.2
Colorado.....	18,817	4.5
Ohio.....	9,845	2.1
Missouri.....	7,674	1.6
Other States.....	53,204	11.5
Total.....	464,494	100.0

^a From statistics compiled by United States Geological Survey.

OCURRENCE OF THE PYRITE.

The principal pyrite deposits of the eastern half of the United States are found in the Appalachian Mountain range in scattered districts from New England to Alabama, the principal commercially exploited deposits being found in northern New York, in Virginia, northern Georgia, and in northeastern Alabama.

Pyrite is also obtained in Missouri, Colorado, and other Western States. California also is a large producer of pyrite.

In southwestern Wisconsin a marcasite ore is found, but the greatest production in that district is obtained as a by-product in the concentration of zinc blende from a mixture of zinc and iron sulphites.

As a general rule, the domestic pyrite ores, when mined, produce more fines than they do lump ore. The average proportion is two-thirds fines and one-third lump. This fact has caused considerable difficulty during the last two years in marketing the pyrite produced in the southern field. The southern pyrite has been primarily fine ore and fine concentrates from milling operations, whereas the greater proportion of the southern plants are equipped for burning lump or furnace ore. The northern pyrite producers, however, have had no difficulty in disposing of their fines as well as their lump ore output, as the furnace equipment in the North consists primarily of fines burners. The distribution of fines and lump burners in the various sections of the country is discussed elsewhere in this report (pp. 63 to 69). A large proportion of the ore in the East must be crushed and concentrated before it is put on the market. The average eastern domestic pyrite—lump, fines, or concentrates—will run about 40 per cent sulphur. An occasional mine or concentrating mill will produce material running as high as 45 or 47 per cent sulphur, and, on the other hand, some material runs as low as 35 per cent sulphur.

The ores as a rule are very low in phosphorus and arsenic. They frequently contain copper in proportions varying up to 2 or 3 per cent, with small amounts of lead and zinc.

The domestic fines and concentrates as a rule are less difficult to roast than the Spanish fines, because the individual grains of pyrite appear to be coarser and there is less tendency for the material to dust and to clog the hearths.

PYRITE MINES IN UNITED STATES.

A brief mention may be made of the mines in the country which have been producing ore recently, or which have made preparation to produce ore within the last year (1918).

New York and Massachusetts.—Prior to 1910 the Davis mine in the Charlemont district in Massachusetts was an important producer, but on account of a cave-in, the production was suspended in 1910. Since then the production in Massachusetts has been practically negligible.

In New York the principal producers during the last two years have been:

1. The mine of the St. Lawrence Pyrites Co., near Herman, in St. Lawrence County. This mine has been producing for more than

10 years. The crude ore runs about 20 per cent sulphur, and the concentrates from the mill run approximately 42 per cent sulphur.

2. The Northern Ore Co., in the Edwards district, St. Lawrence County. Pyrite is produced by this company as a by-product in zinc concentration.

3. The mine of the New York Pyrites Co., near Gouveneur, in St. Lawrence County. The company shipped lump ore during 1918 and is now prepared to ship concentrates.

Virginia.—Virginia has always been the largest producer of pyrite in the East. The principal producing or near-producing mines in Virginia are located east of the Blue Ridge in the central and north-western parts of the State, in a well-defined belt which runs north-east through Buckingham, Fluvanna, Louisa, Spotsylvania, Stafford, and Prince William Counties. There are three producing mines grouped around Mineral, in Louisa County. The principal mines in this State are as follows:

1. Armenius mine, about $1\frac{1}{4}$ miles north of Mineral. Prior to 1916 this mine produced between 50,000 and 60,000 gross tons of lump pyrite and concentrates per year. Its production was reduced to less than 1,000 tons per month by a cave-in of the main shaft early in 1916. This mine is now being operated by the Grasselli Chemical Co.

2. Boyd-Smith mine: Three-fourths mile south of Armenius and 2 miles from Mineral. This mine was operated in 1918 by E. I. du Pont de Nemours Powder Co.; it ships mostly concentrates with a small output of lump ore.

3. Sulphur mine, near Mineral, in Louisa County. This mine was operated in 1918 by the Virginia-Carolina Chemical Co.; it has shipped for 35 years and the principal output now is concentrates and fines.

4. Julia mine, about 1 mile southwest of Mineral. This property was developed in 1918 by the Armour Fertilizer Co.

Other producing mines in the State are:

5. Old Dominion Sulphur Corp. mine, near Garrisonville, Stafford County, Va. The product shipped is a concentrate carrying 47 per cent sulphur.

6. Cabin Branch mines, near Dumfries, Prince William County, Va. This mine, owned in 1918 by the American Agricultural Chemical Co., ships lump ore and concentrates.

Several other deposits were developed to a greater or less degree during 1918, but no production was obtained from them.

South Carolina.—The only producer of pyrite in South Carolina is the mine of the Kershaw Mining Co. in Lancaster County. This mine, which was started early in 1918, has shipped a small tonnage of lump pyrite, but the product is principally a concentrate carrying copper.

Georgia.—Mine of the Chestatee Pyrite & Chemical Corp., at Chestatee, in Lumpkin County. This property was under extensive development in 1917 and 1918. In 1917 the shipments were lump ore, but in 1918 shipments of fines and concentrates were begun. The ore body here is the largest developed in the State. A power plant developing 1,000 horsepower has been installed, and a branch connecting with the Gainesville & Northwestern Railroad at Clermont has been completed.

2. Mine of the Standard Pyrites Co., in Cherokee County, 7 miles southeast of Ball Ground, on the Louisville & Nashville Railroad. This mine produces coarse granular pyrite, which is concentrated to a 45 per cent product. The product is free from arsenic and copper.

3. Mine of the Marietta Mining Co., at Marietta, in Cobb County. This mine produces a granular pyrite which is concentrated.

4. Mines of the Marietta Mining Co., at Villa Rica, in Colt County, developed during 1918.

5. Shirley mine of the Georgia Mining Co., near Hiram, Paulding County. Some ore has been shipped from this mine, but it is still being developed.

6. Little Bob mine, near Hiram, operated by Hanna & Co., of Cleveland. This mine is capable of producing about one-half lump ore; the remainder can be readily concentrated to 40 per cent sulphur.

7. Mine of the Sulphur Mining & Railroad Co., a subsidiary of the Virginia-Carolina Chemical Co., at Villa Rica, Carroll County. This mine has produced for 20 years up to 1918. Some work was done in 1918 toward re-treating some of the old tailings from the concentrator.

Alabama.—1. Property of National Pyrites & Chemical Co., Pyriton, Clay County. Both lump and concentrates are shipped. The ore carries about 1 per cent copper.

2. Carpenter mine, Pyriton, Clay County, owned by the Southern Sulphur Ore Co. In 1918 this mine produced lump ore. However, the fines ore can be concentrated to a suitable product

3. Mattison mine, near Pyriton.

Missouri.—1. Missouri Cobalt Co., of Fredericktown, Madison County, has shipped a concentrate containing copper, cobalt, nickel, and sulphur.

2. "Hobo" mine of the American Agricultural Chemical Co., situated about 6 miles southeast of Bourbon, Crawford County.

3. Cherry Valley iron mine, near Steelville, Crawford County.

4. Beulah mine, 1 mile south of Kelsey, operated by the Commercial Acid Co., of St. Louis.

Much of the ore mined in the "filled-sinks" area, which lies adjacent to the Frisco Railroad between St. Clair and Rolla in Franklin and Crawford Counties, and in which the three last-named mines

are situated, is marcasite, which tends to spontaneous combustion, and is therefore difficult to ship.

Wisconsin.—The Wisconsin district does not produce any large tonnage of raw pyrite, but has an annual production of zinc-iron concentrates, which is shipped to zinc smelters in Illinois, and also a by-product containing about 28 per cent sulphur. This by-product during the last few years has been shipped to an acid plant. The ores in this district are treated as follows: They are crushed and are then given a "flash roast," which oxidizes a small percentage of the total sulphur, practically the volatile atom of sulphur in the pyrite, thereby making the iron sulphide, which remains magnetic. The calcine is then treated under the magnet, and a high-zinc, low-iron concentrate and a magnetic iron sulphide tailing are obtained. The companies that have shipped iron-sulphide tailings are the Vinegar Hill Mining Co., Cuba City, Wis.; the Wisconsin Zinc Co., New Diggings, Wis.; and the Mineral Point Zinc Co., Mineral Point, Wis.

Colorado.—Extensive deposits of pyrite have been developed in various mining districts of Colorado. The Leadville district alone, if properly equipped, could produce a daily output of at least 1,000 tons. The Colorado pyrite is used to some extent by the Western Chemical Manufacturing Co. at Denver, and during the war some small shipments were made to acid plants in Georgia. However, high freight rates have always prohibited general competition at points east of the Mississippi River. The Colorado ore is generally soft and granular; the lump ore decrepitates in the furnace, and therefore can be used only in fines burners.

California.—There are many large deposits of high-sulphur pyrite in California. The principal deposits of pyrite contain copper or gold, besides the sulphur, and the roasting operations from which the acid is made are preliminary to the smelting operations by which the valuable metals are recovered. The principal mines are:

1. Mine of Mountain Copper Co., near Keswick, Shasta County. This mine produces both lump and fines; the ore contains nearly 30 per cent sulphur, and is smelted for the copper and gold content.
2. Dairy Farm mine, in Placer County.
3. Mine of Leona Chemical Co., near Oakland, Alameda County.
4. Mine of Stauffer Chemical Co., near Oakland.

Other States.—Pyrite ores are found in various other States, but the amount produced primarily for acid manufacture is very small and need not be considered here.

CANADIAN PYRITE.

According to the available records, the mining of pyrite in Canada began in 1880, when ores were mined in the Sherbrooke

district, Quebec, for exportation to the United States for the manufacture of acid.^a With the exception of a few years (about the year 1890), until the year 1910 the production of pyrite in Canada was less than 50,000 long tons per year, of which approximately 30,000 tons was shipped into the United States. In the last seven years the production has increased rapidly from 80,000 tons in 1912 to about 300,000 tons in 1917. In 1917 the imports to the United States from Canada were about 180,000 tons, and in 1918 were nearly 225,000 tons. The sulphur content of the Canadian ores shipped during the last several years has been low, averaging not much higher than 37 per cent, though ores from certain districts contain about 40 per cent sulphur.

The following is a list of the companies operating pyrite mines in Canada during the last two years:

Eustis Mining Co., Eustis, Quebec. Office, 131 State Street, Boston, Mass.

Weedon Mining Co., Weedon, Quebec. Office, Portland, Me.

Nichols Chemical Co., of Canada, Sulphide, Ontario. Office: 25 Broad Street, New York, N. Y.

Southern Pyrites Co., North Pine, Ontario. Office: 25 Broad Street, New York, N. Y.

Algoma Steel Corp., Sault Ste. Marie, Ontario.

Canadian Sulphur Ore Co., Queensboro, Ontario.

La Mine de Cuivre et Or., Stratford, Quebec.

Madoc Mining Co., Goudreau, Ontario. Office: 25 Broad Street, New York, N. Y.

Boyd Caldwell & Co., Lenark, Ontario.

Rand Consolidated Mines, Goudreau, Ontario. Office: 853 Elliott Square, Buffalo, N. Y.

The pyrite production in Canada is almost wholly in the hands of United States organizations, and that produced by Canadian citizens is sold chiefly to United States organizations operating in Canada. The greater part of the Canadian export pyrite is not placed on sale in the United States, but is shipped directly to the acid plants owned by the organizations producing the pyrite.

There are unworked deposits in various parts of the country, notably those in the Goudreau mines area, 17½ miles south of Sault Ste. Marie and about 40 miles from Michipicoten Harbor, on Lake Superior. The ores in this area will average not more than 35 per cent sulphur. The development and working of these deposits is largely a question of getting a market for the ores.

The ores from Quebec are used primarily in the New England acid plants; those from eastern Ontario in the Buffalo, Cleveland, and

^a Geol. Survey, Canada, Report for 1886, pt. 5, p. 61.

Pittsburgh districts; and those from northern Ontario in the Chicago district.

Canadian ore when sold on the market is sold usually on the basis of New York market quotations; and these, prior to 1917, were controlled by the price of Spanish ore. During the war the quotations were very irregular and were subject to considerable controversy.

PYRRHOTITE.

As pure pyrrhotite contains only 39.87 per cent sulphur, whereas pure pyrite contains 53 per cent, pyrrhotite ores formerly have not been considered suitable as a raw material for the manufacture of sulphuric acid. However, pyrrhotite has been utilized for that purpose for many years by the General Chemical Co. at its contact acid plant at Pulaski, Va. This is the only plant in the United States where such practice exists.

DEPOSITS.

There are enormous deposits of pyrrhotite in the eastern part of the United States, notably at the following places:

1. Deposit near Katahdin Iron Works, in Piscataquis County, Maine. This deposit was examined by E. S. Bastin, of the United States Geological Survey, in 1918, who reported that it is 2,300 feet long and 300 to 700 feet wide, containing on an average 100,000 long tons of ore for every foot of depth. The ore carries 26 to 35 per cent sulphur, less than 0.01 per cent phosphorous and less than 0.001 per cent arsenic. It is estimated that this ore may be laid down in New York City for about 13.5 cents per unit of sulphur.^a

2. The Gossam mine of the General Chemical Co., at Monaret, Carroll County, in southwestern Virginia. This is the largest developed body of pyrrhotite in the East. The deposit itself can be traced continuously by its outcrop from New River, near Oldtown, northeastward beyond the Betty Baker mine for a distance of 18 miles. The ore is the raw material for the acid plant at Pulaski, and as fed into the roasters at that plant has practically the following analysis:

Analysis of pyrrhotite fed to roasters at Pulaski, Va.

	Per cent.		Per cent.
SiO ₂	6.2	MgO.....	4.2
Fe.....	48.3	As.....	.06
Mn.....	.02	Zn.....	1.25
P.....	.03	Pb.....	.00
Al ₂ O ₃	1.66	As.....	.007
CaO.....	1.56	S.....	30.3

^a News item, Large pyrrhotite deposits in Maine: Eng. and Min. Jour. vol. 104, Oct. 27, 1917, pp. 758-759.

3. Deposits of mixed pyrrhotite and pyrite in the Ducktown district in Southeastern Tennessee.^b The principal developed properties are (1) the Burra Burra property, (2) the East Tennessee and Mary mines, (3) the Isabella Eureka property, and (4) the School Cherokee property. The Burra Burra deposit probably has 10,000,000 tons of ore carrying between 25 and 30 per cent sulphur. This deposit is being worked by the Tennessee Copper Co., the ore being smelted in a blast furnace and the gases utilized for the manufacture of sulphuric acid.

The ores of the East Tennessee mine and the Mary mine are smelted by the Ducktown Sulphur, Copper & Iron Co. at the smelter at Isabella, and the gases converted into sulphuric acid.

In the Isabella Eureka and the School Cherokee deposit, probably 5,000,000 tons, carrying about 29 per cent sulphur, have been blocked out.

BURNING.

As the pyrrhotite contains no free atom of sulphur, it can not be burned in lump burners, and is much more difficult to burn in a fines burner than is pyrite. In fact, it has been found that in order to burn pyrrhotite at all successfully in the ordinary types of fines burners the ore must be crushed to at least 30 mesh. Not only is pyrrhotite much more difficult to ignite, but it has such a low sulphur content that the heat of oxidation has to be conserved in order to carry on the process continuously. At the plant of the General Chemical Co., at Pulaski, the fines roasters are insulated on the outside of the shell with a magnesia-asbestos covering about $2\frac{1}{2}$ to 3 inches thick, the purpose of this insulating covering being to cut down heat radiation and thereby maintain a high temperature in the roaster.

If the ore contains silica, lime, and other bases, there is a tendency at the temperatures which have to be maintained to start the pyrrhotite burning properly, for the ore to sinter or semifuse and thus cause trouble with the operation of the roaster.

On account of the large proportion of very fine ore which is necessarily present if the whole material is put through 30 mesh, the air can not work down into the charge and the oxidation is almost entirely a matter of surface combustion. For this reason the surface should be changed as rapidly as practicable by rabbling. This frequent rabbling also tends to keep the ore from sintering or semifusing.

It is difficult to reduce the sulphur content in the cinder to less than 4 per cent by the ordinary processes of burning, thus the actual

^b Taylor, J. H., Pyrite and pyrrhotite resources of Ducktown, Tenn.: *Am. Inst. Min. Eng. Bull.* 134, Feb., 1918, pp. 529-533.

number of available sulphur units in a ton of pyrrhotite is much smaller than in a pyrite ore. For example, in order to have the same number of sulphur units it would be necessary to handle 1.65 tons of a 30 per cent pyrrhotite as against 1 ton of a 45 per cent pyrite.

In August, 1918, some tests were made at the plant of the Virginia Carolina Chemical Co., at Pinners Point, Va., to determine the feasibility of roasting pyrrhotite in its Hoffman fines burners. These tests were made by D. E. Fogg, of the Bureau of Mines, in cooperation with the staff of the company. The conclusion drawn from these tests was that pyrrhotite ore, when crushed to 30 mesh, can be successfully roasted in an ordinary type of multiple hearth roaster if enough brimstone (approximately 10 per cent) is added to preheat the ore in the top hearth to start ignition there, and if the roaster has some heat insulation to prevent high losses through the furnace walls.

PYRITE FROM COAL ("COAL BRASSES").

In certain districts through the eastern coal fields considerable quantities of iron pyrites occur as bands interbedded with the coal or as balls or nodules in the coal. In some places the bands are several inches thick, up to 5 inches, and are several square feet in area, or they may even form definite interbedded layers with the coal. The balls or segregations are decidedly irregular, both in size and in distribution. The pieces of pyrite as blasted or loosened with the coal in the mine generally have some coal attached, so that the "coal brasses," as they are discarded in the gob piles of the mine or on the dump at the surface, contain usually about one-half coal and one-half pyrite, by weight, and run only 25 per cent sulphur.

In the past, efforts have been made to clean the pyrite of the adhering coal by breaking off the coal with a hammer, the partly cleaned pyrite then being shipped to some acid plant. Such cleaning was inefficient when done by day labor underground and entailed much rehandling when done on the surface. On account of the fact that the product still contained considerable coal it was subject to spontaneous combustion and was therefore an undesirable product to ship. This adverse feature and the fact that acid produced from the partly cleaned brasses was apt to be contaminated with carbon driven off from the adhering coal and carried over into the chambers, tended to prevent the acid manufacturer from purchasing this material, especially so long as a purer pyrite could be obtained. Prior to the war the price received was even less than \$2.50 per ton for material containing 38 to 40 per cent sulphur.

As a rule the hand-cleaned slabs or nodules of pyrite are shipped to the acid plant and allowed to weather for several months. The

adhering coal slacks and if the entire product is then screened or crushed and screened, the coarse oversize is a fairly pure pyrite which does not disintegrate in the furnace, and which contains no arsenic and very little phosphorus. The Indiana and Illinois coal fields have irregularly shipped hand-picked pyrites to near-by acid plants, particularly to those near Chicago, Indianapolis, and Sandusky.

In Danville, Ill.^a for several years a concentrating plant has been treating crude brasses collected from the local coal mines; the product shipped has been a pure pyrite of both lump and fine sizes, analyzing between 45 and 48 per cent sulphur. Some of this product was shipped as far east as Beaver Falls, Pa.

The annual production of pyrite or "coal brasses" from the coal fields of western Pennsylvania, Ohio, Indiana, and Illinois has been about 25,000 tons to 30,000 tons, most of which came from Illinois and was lump material. In 1918, a new plant was built at Gillespie, Ill., to treat about 200 tons daily of crude brasses collected from adjacent mines.

In 1917, when it became evident that there would be a heavier demand for sulphur bearing material than had existed prior to that time, considerable attention was given to the project of increasing the production of coal brasses. The first careful investigation as to the possible supply from the Illinois field was conducted by the Illinois geological survey. The results of this work were given in publications of the State geological survey, by E. A. Holbrook and J. E. Pogue, under dates of August 20 and October 18, 1917. Late in 1917 and in 1918, an investigation covering all the eastern coal-producing States was conducted by the Bureau of Mines, in cooperation with the State geological surveys of Pennsylvania, Ohio, Indiana, Illinois, West Virginia, Kentucky, Tennessee, Georgia, Michigan, and Missouri.

Not only were the most promising sources of supply determined, but tests were made with practically all the kinds of raw material to determine adaptability to concentration processes. The tests were made under the direction of E. A. Holbrook in the laboratories of the Bureau of Mines experiment station at the University of Illinois.

These investigations have shown that from the coal mines in the States mentioned, there may be produced a very large tonnage of pyrite.

The table following indicates the possible yearly production of pyrite from the mines that can easily produce 1 per cent or more of their coal production as coal pyrite:

^a For description of this plant see "The iron pyrite found in coal," by C. M. Young, *Coal Age*, vol. 11, Jan. 6, 1917, p. 9.

Possible yearly production of pyrite containing 40 per cent sulphur from coal mines of the eastern States.

State.	Long tons.
Indiana -----	260,000
Ohio -----	235,000
Illinois -----	225,000
Pennsylvania -----	200,000
Missouri -----	175,000
Iowa -----	140,000
Kansas -----	125,000
Tennessee -----	55,000
West Virginia -----	50,000
Kentucky -----	25,000
Michigan -----	10,000
Total -----	1,500,000

In mining coal this material is now usually separated from the coal and is thrown into the gob as waste. It can be loaded out without much difficulty and be either hand cleaned or treated by a properly designed and constructed concentrating mill from which two pyrite products, lump ore and fines assaying as high as 45 per cent sulphur and containing less than 5 per cent carbon, can be obtained. As a rule the mill will produce about one-half ton of pyrite and one-fourth ton of clean coal per ton of raw material treated. The average recovery of pyrite will be above 85 per cent. Concentration involves crushing, either by rolls or jaw crushers, screening through trommels, and jigging, which may or may not be followed by the use of Wilfley tables. A plant to treat 200 tons of crude material per day cost about \$20,000 in 1918. The cost of operation in 1918 was about 80 cents per ton of raw material. The actual cost of the finished pyrite, of course, will vary with the cost of loading and delivery to the coal tippie, the cost of shipping the raw material to the cleaning plant, and with the grade of the raw material.

From the investigations made in 1918 it was evident that an outside concern going into the business of collecting crude coal brasses would have to pay practically the same price per ton as for coal at the surface. Whether this price for raw brasses will hold in the future is not certain. If the price does hold, of course, it will probably be difficult for an outside concern to produce a large tonnage of pyrite from coal brasses in competition with other sources of sulphur-bearing material, especially as the market for any large tonnage of the product is necessarily east of the Appalachian Mountains, involving considerable freight haulage. However, there is a possibility that the Central States will consume slightly more of the coal pyrite than was consumed prior to the war.

WASTE SULPHUR DIOXIDE GAS FROM ROASTING ZINC ORES.

The manufacture of acid as a by-product from the roasting of zinc blende in smelting zinc ores was introduced in this country about the year 1895, at the plants of the Matthieson & Hegeler Zinc Co., La Salle, Ill., and the Illinois Zinc Co., Peru, Ill. All of the zinc smelters in Illinois, Indiana, Ohio, Pennsylvania, and West Virginia where zinc sulphide ores are being roasted now produce acid as a by-product. There are 16 zinc plants producing by-product acid—12 by the chamber process and 4 by the contact process.

At these 16 plants the material roasted is usually a concentrate containing between 40 and 55 per cent zinc and between 25 and 32 per cent sulphur. The material is roasted in a special type of muffle furnace, described later, until the sulphur content is reduced as low as possible, usually about 1 per cent or less. In order to desulphurize the ore to this extent it is necessary to use external fuel, usually producer gas, this gas being burned out of contact with the ore.

At the zinc plants in Kansas, Missouri, and Oklahoma similar zinc ores and concentrates are being roasted, but until this year (1919) the manufacture of acid at these plants has not been undertaken. The plants were remote from the large markets at the time they were built, and as there was no necessity of utilizing the waste gases, the heavy investments required in the erection of acid plants were not made. If the zinc plants in this district were equipped with acid plants, the production of acid from zinc ores could be increased possibly by 60,000 tons (basis 100 per cent H_2SO_4) per year. One acid plant is now being built in this district.

Except for the fact that the content of sulphur dioxide is lower and more variable in the gases from the zinc-ore roasting furnaces than in the gases from pyrite or brimstone roasters, there is no special difference in the manufacture of the sulphuric acid. However, the lower, variable sulphur dioxide content makes the cost of manufacture higher.

There are also other plants where pyrite ores containing small quantities of zinc are being roasted, but these operations are being conducted primarily for the acid production rather than for the recovery of the zinc. These ores are generally roasted in ordinary fines burners.

WASTE SULPHUR DIOXIDE GASES FROM COPPER SMELTING.

The production of acid by utilizing the roaster gases at copper smelters involves practically nothing new from that of producing acid from ordinary fines pyrite. Usually the roasting must be conducted under more careful control, as regards the air admission, than

where the copper ores are being roasted without the production of acid, for usually the concentration of SO_2 in smelter roaster gases is too low to use in the manufacture of acid. With care, the necessary concentration may be attained.

Sulphuric acid is being made in this manner as a by-product of copper smelting at the following plants:

Garfield smelter, Garfield Smelting Co., Garfield, Utah.

Washoe smelter, Anaconda Copper Mining Co., Anaconda, Mont.

Perth Amboy smelter, American Smelting & Refining Co., Perth Amboy, N. J.

Smelter of the Mountain Copper Co., Martinez, Calif.

Smelter of the Calumet & Arizona Mining Co., Douglas, Ariz.

The copper ores or concentrates at these plants usually carry about 30 to 35 per cent sulphur, although at the plant of the Mountain Copper Co. the ore runs nearly 50 per cent sulphur. As a rule, the sulphur content is reduced to not less than 8 per cent, which leaves sufficient sulphur for the subsequent smelting operations. No external firing is required to carry on the process of roasting these ores.

All of these plants are chamber plants, and with the exception of the production of the Mountain Copper Co., the acid is used largely for metallurgical operations being conducted by the producing companies. As has been stated above, the practice of producing acid by utilizing the gases from roasting copper ores could be greatly expanded in the western States, if there was a local market for the acid. Flotation concentrates, because of their extreme fineness and the tendency to make dust, usually are not as satisfactory for the making of acid as are the coarser products from other concentrating processes, or the crude, heavy sulphide ores.

Acid is being made from the waste gases from copper blast furnaces at only two plants in this country—the plant of the Tennessee Copper Co. and that of the Ducktown Sulphur, Copper & Iron Co., in the Ducktown district, southeastern Tennessee. As the result of an injunction obtained in 1905 by the State of Georgia against these copper companies imposing a restraint on the discharging of sulphurous gases into the atmosphere it was necessary for the companies to take active steps to utilize the waste gases. The operation of a sulphuric acid plant to utilize blast-furnace gases had never before been attempted as the project offered many serious difficulties; among them being the irregular supply of sulphur dioxide gas, variable temperature, large quantities of flue dust, and the large and variable quantities of carbon dioxide present. These difficulties have largely been eliminated or minimized, and acid has been produced in large quantities by the chamber process at these smelters since 1906. The largest plant is that of the Tennessee Copper Co., at

Copperhill, in 1918, this plant produced acid at the rate of about 1,000 tons (50° B. basis) per day. Further description of the practices at these plants appears elsewhere in this report.

SPENT OXIDE FROM GAS WORKS.

The amount of spent oxide from gas works available for acid manufacture is very small in comparison with the other raw materials. However, it may be well to mention this product.

Most works producing illuminating gas from coal purify their product from sulphurous acid by passing it through a mixture of ferric oxide and sawdust. As a result ferrous sulphide and sulphur are formed. On exposure to the air the ferrous sulphide is converted to ferric oxide with the formation of more free sulphur. Spent oxide runs as high as 60 per cent sulphur, and will average 40 to 50 per cent. However, the presence of lime renders part of this sulphur unavailable for acid making. The material is contaminated with ammonium salts and ferro and sulpho cyanides which would interfere with acid manufacture, causing an unduly high consumption of niter. These salts are usually washed out before the spent oxide is used.

Several schemes have been devised and plants erected for leaching the sulphur from the spent oxide by a hydrocarbon, such as benzol, or by carbon bisulphide, and then boiling off the volatile solvent, leaving behind the sulphur with any tars which might be dissolved also.

The product obtained has been 90 to 92 per cent sulphur, the rest being tarry material. This product would not be a desirable material for the manufacture of acid in normal times, but a small tonnage was produced and sold to acid manufacturers during the war.

EQUIPMENT AND METHODS USED IN MANUFACTURE.

The types of equipment used and the processes employed in the manufacture of sulphuric acid in this country are discussed in the following pages.

BURNERS OR ROASTERS.

GENERAL FUNCTION OF BURNERS.

At all sulphuric acid plants, except those where the acid is made as a by-product in copper or zinc smelting, the burners or roasting furnaces are used solely for producing sulphur dioxide gas. Their function is to produce a steady supply of that gas at as nearly constant a concentration as possible and, at the same time, to effect as complete oxidation of the sulphur in the ore as may be possible. The more nearly these two objects are accomplished with a minimum cost for labor and repairs, the more perfect is the burner and its operation.

The production of a steady stream of gas of constant composition is of the greatest importance to the manufacturer of the acid, whether the material being burned is pyrite or brimstone. Inasmuch as nearly all the troubles experienced in acid making come from fluctuations in the sulphur dioxide content of the furnace gases, the more nearly a constant and uniform gas composition can be approached the more nearly will the acid manufacturing process be uniform, and thus become almost mechanical.

Next in importance to the consideration of constancy and regularity of gas volumes and composition is the actual percentage of sulphur dioxide in the gases.

Experience has shown that with pyrite the best results, both in the roasting furnace and in the chamber plant, or in the contact plant, are obtained when the gases leaving the burners contain 7.0 to 7.5 per cent sulphur dioxide. With certain ores this percentage can be somewhat increased with satisfactory results. When burning brimstone, the gases should contain 8.5 to 9 per cent sulphur dioxide.

Often when sulphur dioxide gas is produced as a metallurgical by-product it is not possible to obtain these conditions, either as to constancy of volume and composition or the content of sulphur dioxide

present. In very few instances, however, is it necessary that the metallurgical gas shall contain as low as 4 per cent SO_2 , and usually the gas will contain 5 to 6 per cent SO_2 . Where the sulphur dioxide concentration is lower, it is usually possible, and occasionally commercially practicable, to enrich and steady the gas by burning a rich pyrite ore or brimstone either admixed with the ore or in a separate auxiliary furnace.

In order to maintain the desired regularity of volume and composition of the burner gases it is necessary to insure a uniform supply of ore, and also of air to the furnaces.

REGULATION OF ORE SUPPLY.

In the mechanical furnaces, such as the fines burners or special brimstone burners, a uniform supply of ore is effected by means of an automatic mechanical feed. In the use of hand-worked furnaces, usually a series of such furnaces are charged and discharged at regular intervals so that the average of the gas coming from the series remains practically constant.

Not only is it necessary to regulate the supply of ore, but it is also necessary to have the ore properly sized, and of fairly uniform physical condition. Especially in the operation of lump burners, it is desirable to have ore of uniform size, free from fines or lump above the size for which the furnace grates are set. The burning of the sulphur in lump pyrite is in many ways analogous to the burning of carbon in anthracite. Just as an indiscriminate mixture of all sizes of anthracite, from culm and pea to nut size, can not be burned satisfactorily and evenly, even with care in stoking, no more successfully can pyrite ore of variable size be burned. The spacing of the grate bars in lump burners is also of great importance, as these should be spaced to suit the size of the ore being roasted. The more closely the ore is sized, and the more carefully the grate-bar spacings are adjusted to suit the sizes of the ore, the more uniformly will the roasting proceed, with consequent beneficial effect in the acid plant.

One of the most serious results of trying to roast improperly sized ore in a lump burner is clinkering. In a kiln filled with ore sized with reasonable care, the air comes in contact with all the pieces of ore to about the same extent, and the combustion takes place regularly. However, when the ore contains a considerable proportion of smaller pieces, or fines, there will be some points where the air can not pass. At the temperature of the kiln the sulphur in the particles of pyrite shut off from the air will partly sublime, and the FeS_2 will be converted into FeS , or a fusible matte. This matte will become slightly fused or melted and cause the formation of a clinker. This not only causes the sulphur to be retained in the cinder, but also tends to cause fluctuation in the gas concentration.

REGULATION OF AIR SUPPLY.

With a given type of ore and a constant rate of feed the supply of air should be regulated to within fairly narrow limits in order to realize the best results. Not only should the quantity of air admitted to the furnace be carefully regulated, but there should also be control over the points of admission. In a fines burner, for example, an adequate amount of air should be admitted at the point in the furnace where the most active combustion is taking place, but air should not be permitted to sweep over the cinder after the sulphur content has been reduced to $3\frac{1}{2}$ or 4 per cent. at which stage an excess of air simply serves to cool the ore below its combustion point, and thereby prevents the complete oxidation of the sulphur.

In intermittently charged and hand-worked furnaces the air supply should be regulated in accordance with the sulphur content of the ore in each individual furnace. In a large fuel bed too free a supply of air produces too high a temperature, causing the pyrite to fuse and clinker, a result precisely similar to that attendant upon insufficient air in localized spots.

Because of the importance of a regular air supply, the burners or roaster furnaces are preferably operated on a positive draft induced primarily by a fan placed in the flue system. In chamber plants the fan is usually between the furnaces and the Glover tower, or between the Glover tower and the chambers, and in contact plants, before the scrubbers. By means of the fan it is possible to adjust instantaneously the draft on the furnaces to meet any required conditions, such as variations in the quantity or character of the ore charged.

BRIMSTONE BURNERS.

In burning brimstone for the manufacture of sulphuric acid it is not only necessary to maintain a gas of sufficient richness in sulphur dioxide, but also to prevent sulphur from being volatilized and carried over into the acid plant. Thus the necessity for a positive control of the draft, and a well-regulated control of the feed, is evident.

PAN BURNERS.

The simplest form of sulphur burner is, of course, the pan burner, consisting of a flat-bottomed cast-iron pan covered with a cast-iron or brick arch to form a chamber. Various constructions of this type of furnace are used and produce good results, hence it is hardly necessary to describe them in detail. The pans vary in size from 3 inches to 7 inches deep, 3 feet to 4 feet wide, and 6 feet to 8 feet long. The bottom of the pan is usually slightly dished or inclined,

so that the molten sulphur will collect in a pool nearer the forward end. At one end of the furnace is provided a charging door, hinged at the top. At the other end of the furnace is a connection to the flue. Air is admitted to the furnace through the forward end by keeping the edge of the door slightly raised by means of hand screws.

Provision is generally made for a preliminary heating of the iron pan, and when the furnace becomes hot enough to melt sulphur the sulphur is thrown in and ignited. From then on, the heat generated by the burning of the sulphur melts the fresh sulphur that is thrown in, the molten sulphur spreading over the pan and igniting.

Intermittent feeding of the sulphur in this type of furnace permits a quantity of cool air to be admitted to the furnace, cooling the furnace temporarily and diluting the gases. Therefore various schemes are employed to feed the furnaces through the top arch continuously, or if several furnaces are being operated in a battery, the furnaces are fed in regular order at stated intervals, so that the average gas from the battery will be of reasonably constant strength.

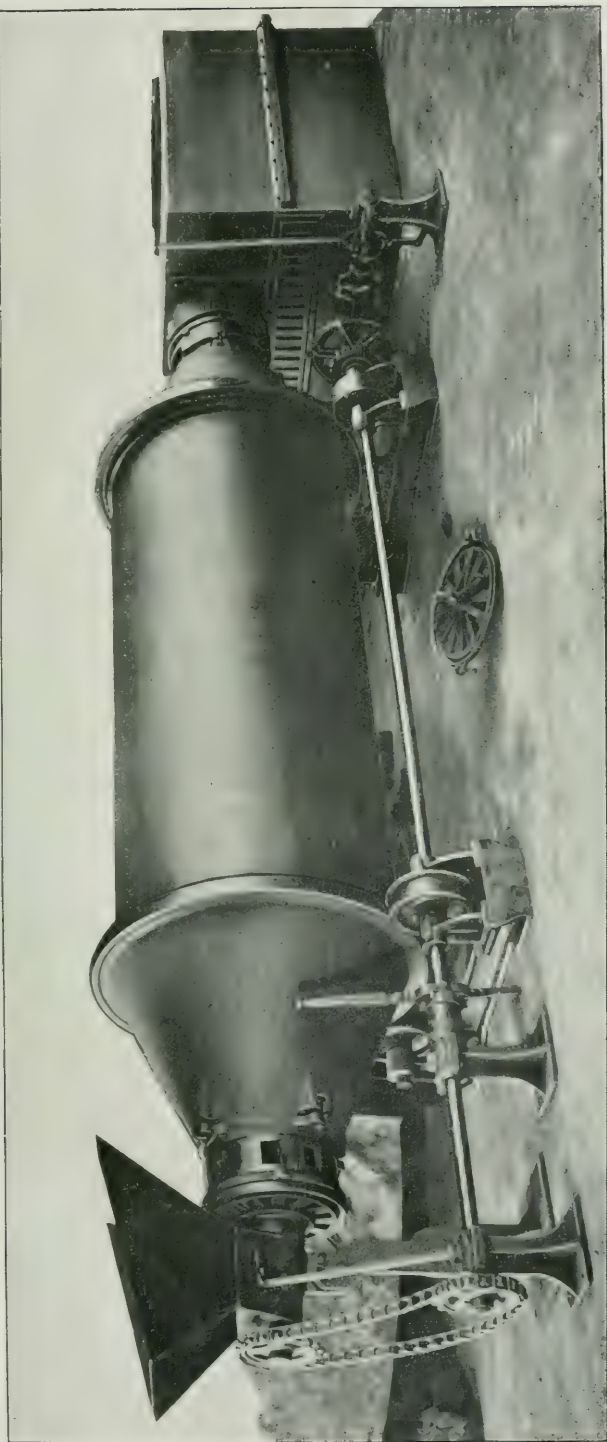
When the sulphur is fed in continuously it is usually first shoveled into a hopper placed near the forward end of the furnace and so constructed that sufficient heat is radiated or conducted from the furnace to melt the sulphur in the bottom of the feed hopper. The melted sulphur can then be discharged into the burner through a spout or pipe, the flow being regulated by means of a valve.

Frequently the pan burners are built with two hearths; the sulphur is thrown or fed into the upper hearth, where it is melted by the heat from the lower hearth and then drops into the lower hearth, where it is burned. Most of the air is admitted to the lower chamber, but provision is also made for admitting more air, if necessary, to the upper chamber for the complete combustion of the sulphur vapors.

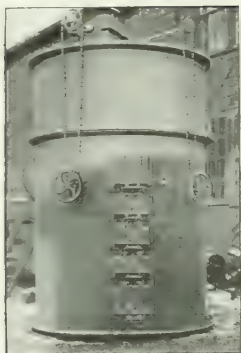
The capacity of a pan furnace is about 1.5 pounds of sulphur per square foot per hour. Thus a large floor space is required for a full installation of pan furnaces. Generally furnaces of this type are used in this country only in emergencies or for short periods, or when it is desired to "boost" the sulphur dioxide content of the gases coming from an ore-roasting furnace.

ROTARY AND VERTICAL BURNERS.

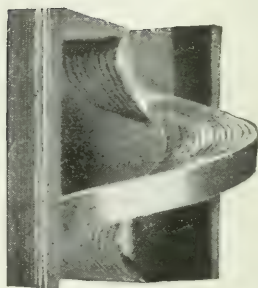
At many plants where brimstone is burned regularly or in large amounts the burner employed is either a horizontal rotary cylinder, such as the Tromblee & Paul burner, or the stationary vertical cylindrical shell containing a series of shelves, such as the Vesuvius burner.



TROMBLEE & PAUL SULPHUR BURNER.



A. VESUVIUS SULPHUR BURNER.



B. SPECIAL RING PACKING.



C. COTTRELL PRECIPITATOR FOR REMOVING DUST AND FUME FROM THREE ROTARY KILNS ROASTING ZINC ORES (BY COURTESY OF RESEARCH CORPORATION).

TROMBLEE & PAUL ROTARY BURNER.

The Tromblee & Paul rotary sulphur burner (Pl. I) is built by the Glens Falls Machine Works, Glens Falls, N. Y. The burner comprises a horizontal, cylindrical flange steel shell, ranging in size from 14 inches in diameter and $2\frac{1}{2}$ feet in length to 48 inches in diameter and 16 feet in length. The ends of the shell are cast iron and are cone shaped. At one end is a hopper and worm feed with sliding dampers. The other end connects with a rectangular cast-iron box, known as the combustion chamber, which is provided with a partition and a vertical cast-iron uptake pipe leading to the flues and to the acid plant. Frequently the combustion chambers are vertical, circular steel tanks with a center baffle wall. The combustion chambers are lined with fire brick. The flanges at the ends of the cylinder form the bearings, which run on rollers or trunnions.

The "standard" size of this burner has a shell 36 inches in diameter and 8 feet long and burns about 250 pounds of sulphur per hour.

The sulphur is fed to the furnace by means of the mechanical worm feed. Before feeding to the hopper, the sulphur needs no other preparation than breaking up the large lumps. When forced along by the worm, the sulphur melts just before it drops into the body of the burner. A bed of burning or boiling sulphur rests in the bottom of the shell. The shell, revolving at the rate of about one-half revolution per minute, performs the function of an agitator, maintaining over its whole inner surface a constantly renewed film of pure sulphur, the surface of which burns intensely. That part of the film underneath the flaming surface protects the shell from deterioration, as sulphur is a very poor conductor of heat.

By a proper adjustment of the dampers on the front end of the burner, perfect combustion may be obtained, and there should be no sublimation of the sulphur. In practice, however, especially where gas of high sulphur dioxide content is being obtained, complete combustion does not always take place in the revolving cylinder, and a certain proportion of the sulphur is volatilized and carried over with the gases into the combustion chamber. Through air tubes, extending into the sleeve connecting the cylindrical burner with the combustion chamber, additional air is admitted for combustion of the volatilized sulphur. Air is also admitted through a space between the burner head and the sleeve, the space being regulated by an adjustable ring.

With this type of burner, control of the composition of the gas between the limits of 4 per cent and 16 per cent sulphur dioxide is a comparatively easy matter, because the feed is continuous and under perfect control, and by proper regulation of air perfect combustion

can be obtained. With Louisiana or Texas brimstone the burner has to be cleaned only about once a month. To do this, or to prepare for a shutdown for repairs in any part of the plant, the sulphur charge is allowed to burn out completely, and any residue in the cylinder is then easily removed with a hoe.

The cost of operation is low, as one man can take care of several furnaces. The cost is usually less than 50 cents per ton.

VESUVIUS VERTICAL BURNER.

The Vesuvius burner (see Pl. II, A) is constructed by the Valley Iron Works Co., Appleton, Wis. This furnace is of the round vertical type, the top of which forms a dome called the "cupola." On top of the dome and partly within the burner is a melting kettle. The shell of the burner is of iron and steel, and is lined with fire brick. The inside of the burner is provided with a number of dish-shaped iron trays or shelves. For each shelf and the bottom compartment a door is provided for regulating the admission of air and for cleaning.

The sulphur is placed in the melting pot at the top of the furnace, where it melts and drips through a needle-point valve in the bottom of the melting pot onto the top tray or shelf. From the top shelf the sulphur drips onto the next lower shelf, then flows across that shelf and drips onto the third, continuing to flow back and forth and drop from shelf to shelf until it enters the bottom chamber of the burner, where the ashes and impurities collect. The following procedure has been found to be satisfactory for maintaining a pool of sulphur on all the shelves and giving a constant gas concentration: The needle valve is opened and the molten sulphur allowed to rush down until it overflows the bottom tray and flows into the bottom; then the needle valve is closed. The operation is repeated at intervals, depending upon the action of the burner. In case a smaller amount of sulphur is required to be burned, say five tons in a nine-ton burner, the same procedure is followed, except that the needle valve is closed when the sulphur commences to flow on one of the shelves higher up, say the third shelf.

The gas outlet consists of two parts—the first part is an elbow extending about $4\frac{1}{2}$ inches into the burner, this extension forming an arch for the brick lining; the second part is a round iron pipe, oblong shaped on one end to conform with the shape of the elbow, the upper end being slotted and serving as a combustion chamber. Around the slotted pipe, resting on projecting rings, is a circular damper which regulates the admission of air so that any sulphur carried out of the furnace proper as volatilized sulphur will be completely burned in the combustion chamber. With proper regulation of the admission

of air onto the shelves and the admission of air to the combustion chamber there should be no loss of sulphur even when a gas of very high sulphur dioxide concentration is obtained.

With a good grade of brimstone, the Vesuvius burner requires cleaning only once in about two weeks, the operation requiring about two hours.

One of the possible advantages of the Vesuvius type burner over the rotary type burner is that the former, being vertical, requires less floor space. A Vesuvius burner having a capacity of nine tons per day requires about 72 square feet of floor area. A rotary burner of the same capacity requires about 300 square feet. The Vesuvius type burner requires no power and thus no expense for oil, belt, or chain. On the other hand, the feed to the vertical type is not continuous, and some difficulty has been experienced in keeping the feed open, as sediment gets into the needle valve, clogging it. Both furnaces require about the same amount of labor or attention to operate.

LUMP BURNERS.

Lump burners are nothing more than the simplest form of a deep-bed coal fireplace. They are rectangular in horizontal section, varying in area from about 18 to 36 square feet, the usual width being 5 feet and the depth from front to back 4 to 6 feet. The burners are usually erected in batteries of 16 to 32 furnaces, the units being arranged in two rows, back to back, with a common central wall. By this arrangement is realized the maximum economy of space, material, and first cost, and the heat losses are reduced to a minimum. There are many different types of furnaces in use, but the following general statements will cover the description of burners of modern construction.

The batteries of furnaces are usually built of brick, common brick being used for the lower part and for the outer walls, and fire brick being used for the inside walls above the grates, for the arches, and for the gas flues. The front walls are usually one tier of brick $4\frac{1}{2}$ inches thick, and are faced with cast-iron plates, one for each unit in the battery, each plate being provided with the necessary openings for operating the furnace.

The center wall between each pair of furnaces is usually two bricks (nine inches) thick, and the side walls between adjacent burners are two bricks thick to a little above the level of the gate, and above that is one brick thick. The end walls of the battery are usually about 18 inches thick, and are faced with solid plates.

The whole battery of furnaces is bound together by vertical buckstays, steel rails, or I beams, held together by horizontal tie-rods which are provided with turnbuckles to permit adjusting the tension to suit the condition of the furnace.

The interior of each unit is divided into two parts by the grate bars. The cinder pit below the grate bars varies from 18 inches to 24 inches in height. The height of the abutments of the arch above the grate bars is about 42 inches, and the spring of the arch is between 8 inches and 10 inches. In some batteries the arch is sprung from side to side over each furnace, on others an arch is sprung from each front wall to the median wall, thus running lengthwise of the furnaces.

The grate bars are usually made of 1½-inch or 2-inch square iron resting on cast-iron bearing bars. Bearings are turned on the grate bars, the diameter of the bearing cylinders being that of the bar. The ends of the bars projecting beyond the first bearing are left square and a key is provided for shaking and turning. The grate bars are spaced 4 inches center to center, usually with the diagonal of the square section horizontal, making an opening between the bars 1.17 inches wide.

To remove part of the cinder it is only necessary to turn the grate bars slightly, one at a time by the key, which is adjusted over the square end. The movement momentarily enlarges the opening between the bars, and forces downward between the bars the cinder lying immediately adjacent to the grate. The whole bed of pyrite above is more or less shaken, or loosened by the grate movement.

The cast-iron fronts of the furnace units are provided with suitable openings for charging the furnace, removing the cinder, and fitting the key on the ends of the grate bars, and gaining access to the flue. Occasionally a poke hole is also provided. The sill of the charging doors is placed about 30 inches above the grate bars, the height of the door varying between 20 inches and 30 inches.

The gas flue is usually built on top of the furnace, the upper part of this being made by a second arch rising 8 inches to 12 inches above the furnace arch, and running the length of the battery. A small opening admits the gases into the flue from the furnace.

In the construction of any type of furnace care must be taken to make all flues or openings into the flues perfectly tight, because all air admitted to the burner or flues, except when it will aid combustion and will be under complete control, is of great detriment.

In most furnaces the doors run in grooves, but in some they are hinged to lugs cast on the plates. When doors run in grooves their faces are inclined, carefully planed, and are pressed by gravity or latch against the planed edges of the door jamb, making a gas-tight joint and rendering the use of luting unnecessary.

Usually the ash-pit, or cinder-pit, door is perforated with 1-inch holes, which can be plugged to regulate the admission of air below the grates.

In lump burners of modern construction the capacity of a single furnace is about 1.8 pounds of 45 per cent sulphur ore per square foot of grate per hour. The charge is thrown in intermittently by hand through the charging door, and distributed as quickly as possible over the surface of the fire bed. To get the most steady gas volume and concentration, and the most complete desulphurization of the ore, it is necessary that the size of the ore pieces and the spacing of the grate bars should be properly regulated. The shaking of the grate bars is done by hand. Alternate bars across the burners are generally shaken, and the intermediate bars are shaken at the next period with such additional treatment as is required to bring down the cinder evenly. The cinder is generally allowed to accumulate in the ash pit, and is removed once every 24 hours.

The depth of the bed maintained on the grates largely depends on the draft conditions and the size of the ore pieces; it varies up to $2\frac{1}{2}$ feet. No red-hot cinder should ever come through the grate bars; in fact, with a proper regulation of the depth of fuel bed, the cinder when shaken down should be fairly cool.

The average cost of roasting ore in a lump burner at a plant roasting over 30 tons of ore per day is about \$1 per ton.

FINES BURNERS.

For the burning of fines ores the cylindrical multiple-hearth furnace of the so-called McDougal type is generally employed in this country. Various modifications of the multiple-hearth furnace have been evolved and patented. Those most commonly used are the Wedge and the Herreshof furnaces. The Skinner furnace and the Hofman furnace are also employed in several plants, these furnaces differing from the Wedge and Herreshof furnaces only in certain details.

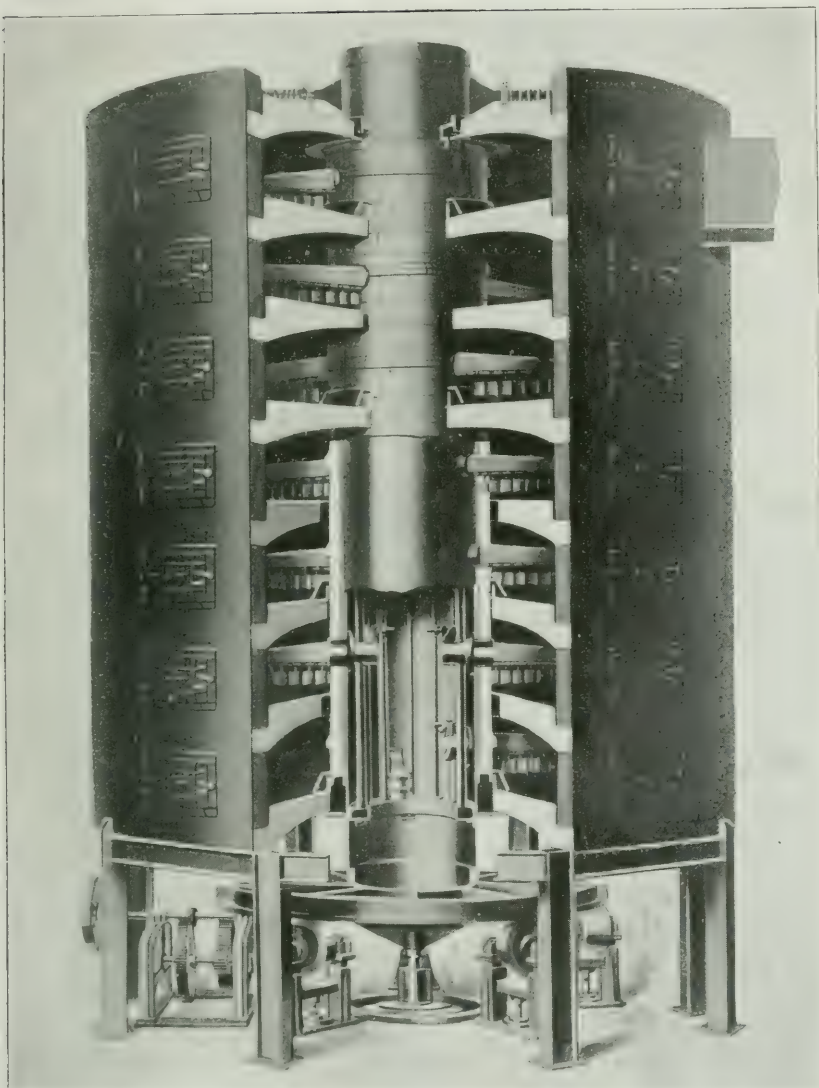
Described briefly, this type of furnace has a vertical cylindrical steel shell lined with common brick or fire brick and contains a series of horizontal or slightly arched brick hearths. In the center of the furnace is a vertical revolving hollow shaft to which are attached removable cast-iron arms carrying replaceable rabblers, these arms revolving over the hearths and rabbling and pushing forward the ore on the hearth. The rabble arms and center column are cooled by air or water. The ore is fed mechanically onto the top hearth at the circumference, from whence it is pushed by the rabblers to the center, then drops onto the hearth below, where it is turned

over repeatedly by another set of rabblés placed at such an angle that the ore is gradually pushed to the circumference to drop through a slot onto the third hearth, continuing in this manner through the furnace until discharged from the bottom hearth into a hopper below the furnace. The rabblés are so arranged in regard to their pitch and progression that a moving layer of ore, in a uniform system of furrows, equal in depth from the center to the circumference is maintained on all hearths. The air for combustion either enters cold through adjustable openings in the doors, or through slots in the rabblé arms, or through special pipes or connections.

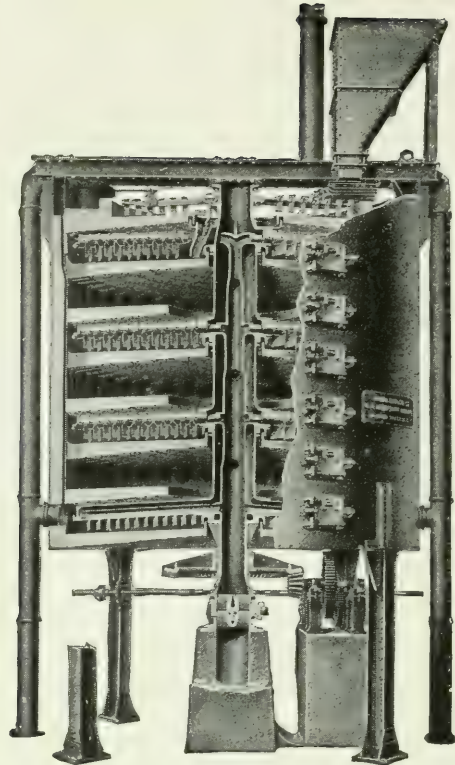
When ores containing 30 per cent or more sulphur are roasted the heat from the burning of the sulphur and the oxidation of the iron is sufficient to carry on the process continuously: the hot gases rising from the hearths, where the oxidation is the most rapid, serve to heat up and start the ignition of the fresh ore descending through the furnace. In fact, with ores containing more than 40 per cent sulphur the temperature of the furnace is apt to become too high at certain hearths, tending to cause fusion of the ore and deterioration of the metal part exposed to the heat. Various means have been devised for controlling the temperature on the hearth, involving the cooling of the rabblé arms with water or air, providing outlets direct to the flue for a portion of the gases at various hearths, and regulation of the air admitted to the hearths.

One of the principal problems in roasting high-sulphur ores is to keep the main shaft and the rabblé arms at a temperature where the metal is kept cool and is not deteriorated. The common practice has been to circulate water through the shaft or arms. This water removes a certain amount of heat from the hearths and thus partly serves to cool them. However, the salts in the cooling water tend to form incrustations in the arms and columns, and, primarily for this reason, there has been a development of air-cooling systems. In these systems air is forced at a pressure of 1 to 3 ounces by means of a fan into the arms or into the main shaft and arms: thence the heated air is discharged directly into the furnace or allowed to escape to the atmosphere, or all or part of the heated air is conducted to certain hearths of the furnace to aid combustion there.

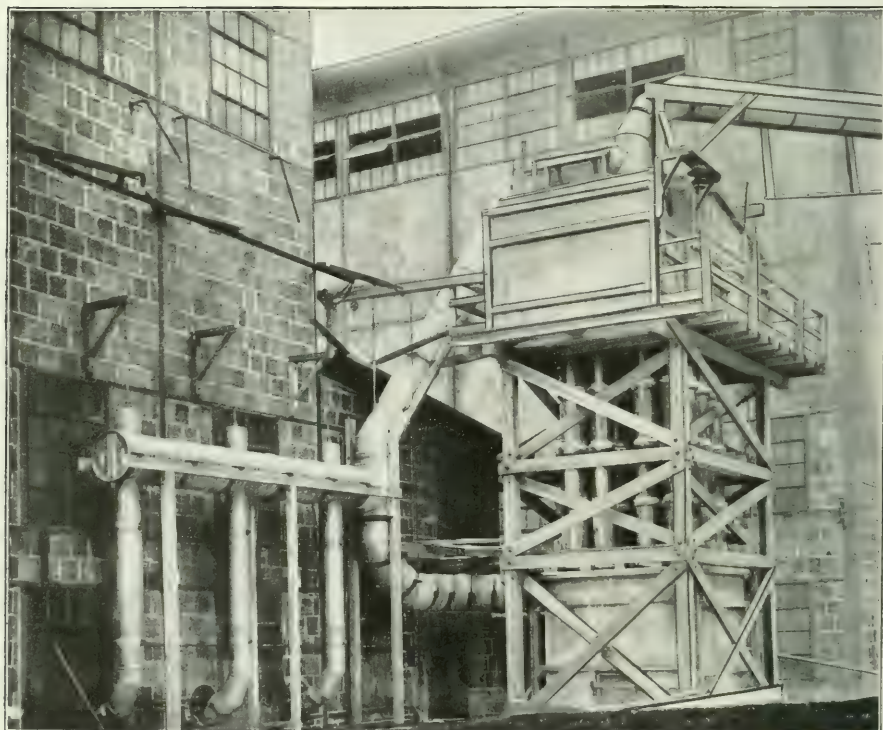
With a well-constructed and well-insulated furnace, equipped with temperature control and under proper care in the regulation of the air supply, etc., it is possible to roast ores containing less than 30 per cent—even as low as 25 per cent—available sulphur to a cinder containing less than 4 per cent of the sulphur, and obtain at the same time a satisfactorily high content of sulphur dioxide in the gases. However, there are very few acid plants in this country where this is being done successfully and as a regular procedure. The most



WEDGE FINES ROASTER.



A. HERRESHOF FURNACE.



B. ELECTRICAL PRECIPITATOR FOR REMOVING ACID MIST FROM THREE SULPHURIC ACID CONCENTRATORS PRODUCING A TOTAL OF 50 TONS OF 66° B. ACID IN 24 HOURS.
(By courtesy of the Research Corporation.)

notable example is at the plant of the General Chemical Co., at Pulaski, Va., where a pyrrhotite ore containing only about 30 per cent total, or less than 25 per cent available, sulphur is being treated in well-insulated Herreshof furnaces.

Mechanically the operation of a fines burner is extremely simple, consisting of feeding the ore regularly and controlling the admission of air to the various hearths to obtain the proper temperature and gas concentration. Regulation of the speed of the furnace to meet the conditions of the ore is also necessary to obtain the desired results.

Oxidation is partly effected when the ore drops from hearth to hearth through an ascending current of heated gases containing oxygen. The rate of oxidation during this period of falling could be largely increased by increasing the velocity of the gases through the openings, but it is necessary to keep the gases at a fairly low velocity to prevent the raising and carrying away of very fine dust particles.

No accurate statement as to the capacities of furnaces in pounds of sulphur or tons of pyrite per 24 hours can be made without a knowledge of the chemical composition or physical character of the ore to be roasted. In general, these furnaces will oxidize 0.5 to 1.0 pounds of sulphur per hour per square foot of hearth area from pyrite ore 40 per cent or higher in sulphur, to 2.5 or 3 per cent sulphur in the calcine.

WEDGE ROASTER.

The Wedge fines roaster (Pl. III and fig. 2) is built by the Wedge Mechanical Furnace Co., of Philadelphia, under patents controlled by it. One of the distinctive features of the Wedge roaster is the large central vertical shaft, which is 5 feet in diameter. This shaft is constructed of $\frac{1}{2}$ -inch steel plate, protected by special fire tile which are attached to and revolve with the shaft. This central shaft, together with the master gears, is carried by six large rollers and their supports, and is revolved by pinion and train of gears and pulley. The removable arms are connected with the main shaft in such a manner that they lock on the inside of the shaft, thus allowing the removal and replacement of an arm without appreciably cooling the inside of the furnace, as workmen can work in the shaft even when the furnace is hot. This large column also permits of independent air or water supply pipes with valve control to each arm or a combination of arms as desired. When air is used for cooling, if the ore does not contain enough sulphur to burn satisfactorily or rapidly, it is possible to assist the "heat balance" of the furnace by discharging the hot air from the arms directly into the furnace

through slots in the arms. Furthermore, as it is not necessary to cool the central shaft, there is no local cooling in the center of the furnace as would be incident to the presence of a cooled shaft there.

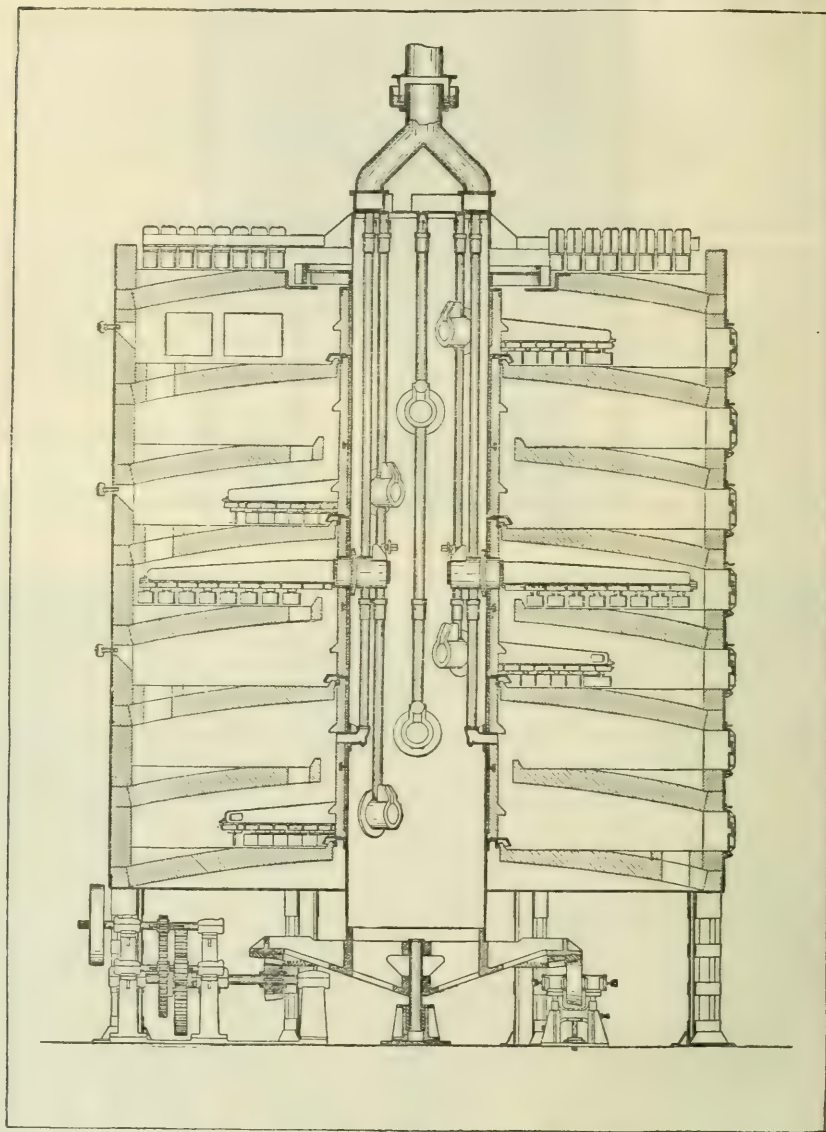


FIGURE 2.—Section through Wedge fines burner.

The rabble arms and blades are the only iron parts exposed to the heat and furnace gases, as the center column is protected by a special tile and a special type of brick.

The Wedge furnaces are built in various sizes ranging from 16 to 25 feet in diameter, and with various numbers of hearths, so that it is possible to obtain the desired hearth area in the smallest number of units. A furnace designed to roast the ordinary pyrite ore containing 35 per cent or more available sulphur does not need special description, as these furnaces are standard in design and construction. The ordinary 20-foot seven-hearth furnace with top drier hearth can be relied on to burn about 50 to 60 tons of pyrite per day when roasting ore carrying 45 per cent or more sulphur to 2 to 4 per cent in the calcine, and to deliver a gas carrying about 7.5 per cent sulphur.

Various modifications of construction are possible to meet special conditions of ores and of results desired.

It may be of interest to note the type of construction recommended by the Wedge Furnace Co. for a furnace to roast an ore containing less than 30 per cent available sulphur. For a daily capacity of 33 tons of such ore, a 25-foot diameter furnace is recommended having seven roasting hearths and a drier hearth. Part of the rabble arms are water-cooled and part are air-cooled. The air, delivered by a fan, enters the furnace at the top of the central shaft and through six 4-inch pipes enters six arms in the upper part of the furnace. The heated air from these six arms is then introduced into six arms in the lower part of the furnace, two arms being in tandem. From these lower air-cooled arms the heated air is permitted to enter the three lower hearths through openings in the outer ends of the arms. The fourth and hottest hearth has water-cooled arms, the water being supplied by gravity from a water pan at the top of the central shaft, which also acts as a lute for the air coming from the fan.

In order to conserve as much as possible the limited amount of heat units generated by the burning of the ore, the outer walls of the four upper hearths have a thickness of $2\frac{1}{2}$ inches of an insulating material, such as "nonpareil" brick or "silocel" brick. The three lower hearths, where the smallest amount of heat is generated, have a thickness of 5 inches of insulating material.

The central shaft is insulated by 4 inches of special tile and $2\frac{1}{2}$ inches of nonpareil brick.

The bottom hearth is supported by a $\frac{3}{16}$ -inch steel-plate floor and I beams, which also support the water lute at the bottom of the central shaft. The bottom hearth is also insulated with nonpareil brick.

HERRESHOF FURNACE.

The Herreshof furnace was developed by the General Chemical Co. through its Herreshof furnace department. The latest pressure air-cooled furnace (Pl. IV, A, p. 67) was developed only during the last five years. In this type of furnace the center vertical shaft is

made double, the outer shaft or tube being of cast iron and the inner tube also of cast iron or of steel. The rabble arms are also made with this double effect, the inside tube of the arm connecting with the inside tube of the shaft, while the outside tube of the arm connects with the outside tube of the shaft. The air supplied by the fan enters the inner tube of the shaft, passes through the inner tube of the arm, thence through the outside arm and shaft tubes to the top of the furnace. Here it is either discharged to the open air or is carried to the bottom or cooler parts of the furnace for combustion, either through temperature-control flues or the bustle pipe, or both.

The temperature-control flues transmit the excess heat from the hottest zones of the furnace to the cooler zones.

Damper control in the waste-heat bustle pipe and in the control flues makes possible the use of as much or as little of the waste heat as is desired. This flexible control makes the furnace adaptable for burning various grades and quantities of ore within reasonable limits. The Herreshof furnace is built in four sizes, the smallest being 11 feet 7½ inches in diameter, the next larger 15 feet 9¼ inches in diameter, the third 20 feet in diameter, and the largest 21 feet 6 inches in diameter, with either five or seven hearths. The smallest size (five-hearth) furnace will roast about 5 tons and the largest as much as 70 tons a day of pyrite from an initial sulphur content of 45 per cent to a final content of 2.5 to 3 per cent.

The cost of roasting in a fines burner varies between \$0.50 and \$1.50 per ton, depending largely upon the size of the plant and the equipment for handling the ore mechanically. During the year 1918 an average cost was about \$1 per ton.

ZINC-ORE ROASTERS.

Zinc blende is roasted primarily to prepare that material for subsequent metallurgical treatment by which the zinc is reduced to the metallic state. As the first consideration in the roasting of blende is to get as complete desulphurization of the material as possible, the production of sulphuric acid from the roaster gases is ordinarily a by-product operation and of special consideration.

Zinc blende as handled at the zinc plant ordinarily contains about 25 to 30 per cent sulphur. Under proper conditions a nearly complete roast of an average blende can be obtained, and one of the conditions necessary is to raise the temperature of the ore to between 700° and 800° C. in contact with sufficient oxygen. Theoretically sufficient heat can be obtained by the oxidation of the sulphur and metal, provided the gases leaving the furnace contain at least 5 per cent sulphur dioxide, to carry on the process without external fuel. However, no furnace has yet been constructed to util-

ize fully the heat of combustion of the ore, and it has been necessary to apply external heat.

The fuel requirements figured to bituminous coal vary between 8 and 35 per cent of the ore roasted. For certain districts, namely, in the Kansas, Oklahoma, and Arkansas zinc districts, the ores are roasted in single-hearth reverberating type furnaces, such as the Ropp or Zellweger furnaces, where the products of combustion of the burning fuel come in direct contact with the ore and thus dilute the sulphur dioxide in the gases leaving the furnace to a point so low that it is not feasible to make acid therefrom. These furnaces are much cheaper to construct than the muffle type, and can be operated much more economically, especially with natural gas, which is available in the district where these roasters are used.

HEGELER TYPE FURNACES.

Where sulphuric acid is to be made from the waste gases the ore is roasted in a muffle type of furnace, of which type the Hegeler furnace is the most commonly used in this country. The term Hegeler furnace does not imply a furnace of a certain definite structure; it refers only to a very general type. The original Hegeler patent (U. S. patent No. 303671) was applied for in 1882, and at present almost every Hegeler furnace has been built differently. There are now several different systems of firing, and several systems of air regulating, besides a great many different designs of minor features. For a detailed description of the Hegeler furnace and the method of operation in order to get the metallurgical results desired, the reader is referred to the book by Ingalls.^a

Hegeler furnaces have seven hearths, the three lower being heated with producer gas (see fig. 3).

The hearths, with muffles, are arranged on each side of the center wall, the concentrate being fed in at opposite ends of the two top hearths and discharged at the two opposite ends of the bottom hearth. The passage of the blende over the hearth is effected by means of a rabbling mechanism. Rabbling is commenced at the top hearth, the charge being moved from the feed toward the discharge end, where it is dropped through a slot in the floor of the hearth upon the hearth below. It is then drawn by another rabble toward the opposite end, where it is again dropped through another slot to the next lower hearth, and so on until discharged from the lowest hearth. The rabble used is a rake type designed to turn over, plow, and move the charge forward through the furnace. The rabbles are supported at the end of the furnace on a stand, which may be moved from one side to the other for rabbling each of the two hearths on each level.

^a Ingalls, W. R., *Metallurgy of zinc and cadmium*, 1903, p. 145.

The rakes are drawn through the furnace by means of detachable rods.

The gas travels in the opposite direction; it is admitted to the lowest fire muffle at one end and passes to the other end, being partly burned by the admission of air at intervals. The gas then passes outside of this muffle, and is admitted through a by-pass to the next muffle above, where it is further burned, the combustion being finally completed under the third muffle.

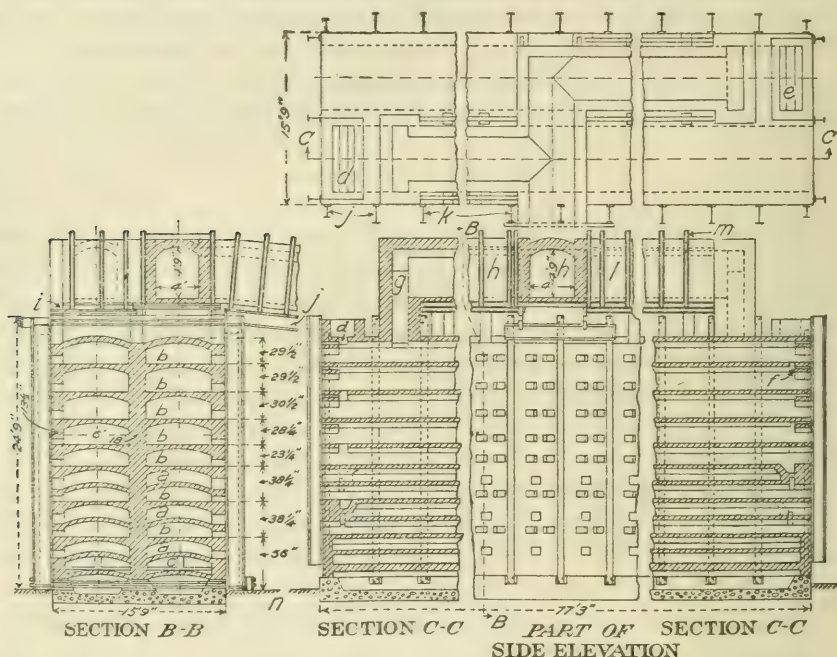


FIGURE 3.—Hegeler furnace for roasting zinc ores. *a*, Fire muffles; *b*, roasting muffles; *c*, muffles for preheating the air; *d*, *e*, feed hoppers; *f*, discharge into second muffles; *g*, flue for gases; *h*, flue to acid plant; *i*, 6-inch I-beam; *j*, 15-inch I-beam; *k*, 20-inch I-beam; *l*, flue; *m*, steel rails; *n*, kiln floor.

The hearths are closed at the ends by sheet-iron doors which are hinged at the top and are automatically opened and closed by the passage of the rabblers through the furnace.

When a Hegeler furnace is running on zinc blende alone, the gases from it seldom carry 5 per cent SO_2 , the SO_2 content is more frequently nearer 4 per cent, and varies considerably.

The costs of roasting zinc blende in a Hegeler type of roaster at different plants and the roasting results obtained vary greatly, depending largely upon the skill of the operators. Prior to the war the working cost of a number of Hegeler furnaces was less than \$2 per ton of ore treated, and averaged throughout the country about \$2.50 per ton.

The first cost of a furnace with all the accessories, on a prewar basis of cost, was about \$1,000 per ton daily capacity of blende roasted.

SPIRLET FURNACE.

Another type of blende roasting furnace used in connection with acid plants is the Spirlet. This type of furnace is used principally in Europe, but also is used in this country by the Grasselli Chemical Co., by the American Zinc, Lead & Smelting Co. at East St. Louis and Hillsboro, Ill., and by the National Zinc Co. at Argentine, Kans. At the latter plant a special construction has been developed for overcoming some of the mechanical troubles present in the operation of the original furnaces.

The Spirlet furnace has several rotating hearths, projections on the underside of one making the rabblers for the hearth beneath. These rabblers are made of special fireclay shapes, which can be removed only by closing down the furnaces and cooling them. The lowest hearth is muffled. The roasted ore is discharged from the periphery of the lowest hearth into a hopper where part of the heat is utilized to preheat the air, the remainder of the heat being supplied from a coal fire in a fire box.

According to Chase,^a the Spirlet furnace requires about 10 per cent of coal as fuel, requires about 2 horsepower to operate a 5-ton furnace, and gives a gas high in SO_2 with a loss of 1 to 2 per cent zinc in the dust.

WEDGE (MUFFLE) FURNACE.

The combination muffle and reverberatory Wedge furnace has also been used for roasting zinc ore. In this type of roaster the heating over the upper hearths is by combustion of the ore. On the lower hearths the ore is heated by coal burned in an external fire box, the combustion gases coming in direct contact with the ore, but not mixing with the gases coming from the upper hearths.

DUST CHAMBERS AND FUME COLLECTORS.

In fines burners there is always considerable dusting of the very fine particles of ore, especially as the ore falls from floor to floor, and even when the burner is so designed as to permit the gases to rise at low velocities through the drop holes a certain amount of this very fine dust is carried out of the furnaces with the gases. There are also present volatilized metals or metallic compounds which are condensed as the gases are cooled, and as the particles of condensed fume are extremely fine, they are easily carried along by the gas streams.

^a Chase, M. F., Choice of a blende roasting furnace: Eng. and Min. Jour., vol. 104, Oct. 20, 1917, pp. 698-704.

The greater part of the mechanically carried dust must be removed from the gases before they go into the Glover towers of a chamber plant or to the scrubbing towers of a contact plant; otherwise the towers will soon be so filled by the dust that passage of the gases through them will be seriously impeded.

METHODS OF MECHANICAL PRECIPITATION.

The method most commonly employed for removing the mechanically carried dust is to pass the gases through a dust chamber or large flue where their velocity is greatly reduced and the dust settles out. Formerly it was believed that passing the gases through a long system of pipes or flues of such cross section that the velocity would not exceed 20 or 30 feet per second would permit settling of all the dust. Modern construction of dust flues or chambers permits reducing the velocity of the gases to not more than 5 feet per second and even less than 3 feet per second, the length of the flues being much less than formerly. A chamber 125 feet long will allow most of the pyrite dust to settle at a velocity of 3 feet per second.

At a chamber plant it is usually desirable to settle the dust with as little loss of temperature as possible, so that long flues are not satisfactory. Hence, various means have been tried for increasing the rate of settling within a comparatively short distance of travel and thus reduce the length of the flues. For example, some settling chambers are constructed with baffle walls or plates placed directly across the path of flow of the gases, with space at the top or bottom of the walls for the passage of the gases. The passing of the gases through these open spaces, however, sets up eddy currents which tend to keep the dust in circulation and thus neutralize to a large extent the effect of the baffles.

Hanging wires in the flues are effective in removing dust particles, and flues hung with wires will allow a satisfactory high dust recovery, even with a velocity of 6 to 8 feet per second. Usually the wires are hung 3 or 4 inches apart and the rows of wires are staggered so that there will be ample provision for the gases to impinge on the wire surfaces.

In the Gilchrist rod collector, constructed by the Chemical Construction Co., iron rods are used in place of wires. Arrangements are provided for vibrating the rods at definite intervals, which shakes the dust to the floor of the dust chamber.

The dust chambers or flues at modern chamber plants are now usually of brick, rectangular in cross section, with an arched roof. At contact plants or chamber plants where it is not so desirable to save all the heat possible they may be made of sheet iron. Frequently the flues are elevated, being supported by a steel structure, and the bottom is made up of a series of hoppers, whence the dust is discharged into cars run beneath.

Centrifugal force is applied in some plants to remove suspended particles from the gases. In the method generally used the gas is brought tangentially into a stationary container of circular horizontal cross section and withdrawn vertically upward through the axis of the container, as in the well-known type of cyclone dust catcher. The dust particles tend to be thrown out to the periphery and finally drop down into a receptacle provided for them beneath. This method is decidedly effective in removing fairly coarse dust, but its efficiency falls off very rapidly in dealing with smaller dust particles.

A dust collector was devised by Henry Howard (U. S. patents 970053 and 896111) having a series of horizontal parallel shelves spaced an inch or so apart, across which the gases pass in a slow stream from one chamber to another, the dust being deposited on the shelves. The dust is then removed by rabbles inserted through doors in the flue walls. With hot gases these shelves tend to warp, which makes cleaning difficult.

None of the above outlined methods for settling dust will remove metallic fumes. As previously stated, the fume particles are so extremely minute that they do not settle from the gas stream by gravity as do the flue-dust particles. Even though the gas stream is cooled so that complete condensation can take place and the velocity of the gases be reduced to a low rate, very little settling of fume occurs. Usually the fume consists of oxidized arsenic, zinc, or lead compounds. At only a few chamber plants, however, is the amount of this fume present in the gases so large that its presence is a serious factor. At contact plants special scrubbing and filtering devices are employed, as described in a subsequent connection, for completely removing these substances from the gases.

The method of removing dust and fume by filtration through cotton or woolen bags, as is employed at various metallurgical plants, has been suggested, but can not be utilized to remove dust from gases from pyrite burners because the sulphuric acid anhydride (SO_3) or sulphuric acid mist present would destroy the bags and because the temperatures are very much too high.

The use of fine wire screens and of asbestos in place of cotton or woolen fabrics has also been suggested and tried, but they have not proved serviceable, chiefly because of their high cost, clogging of the pores, rapid corrosion of the wires when fine enough to filter effectively, and the tendency of the asbestos to become brittle in highly acid atmospheres.

ELECTRICAL PRECIPITATION.

During the last few years several electrical precipitation units have been installed at acid plants for removing both the dust and the fume from the gases.

Plate V shows the interior of an electrical precipitation unit; Plate II, *C* (p. 61), shows an exterior view of a precipitator; and figure 4 shows the general arrangement of a precipitator installation.

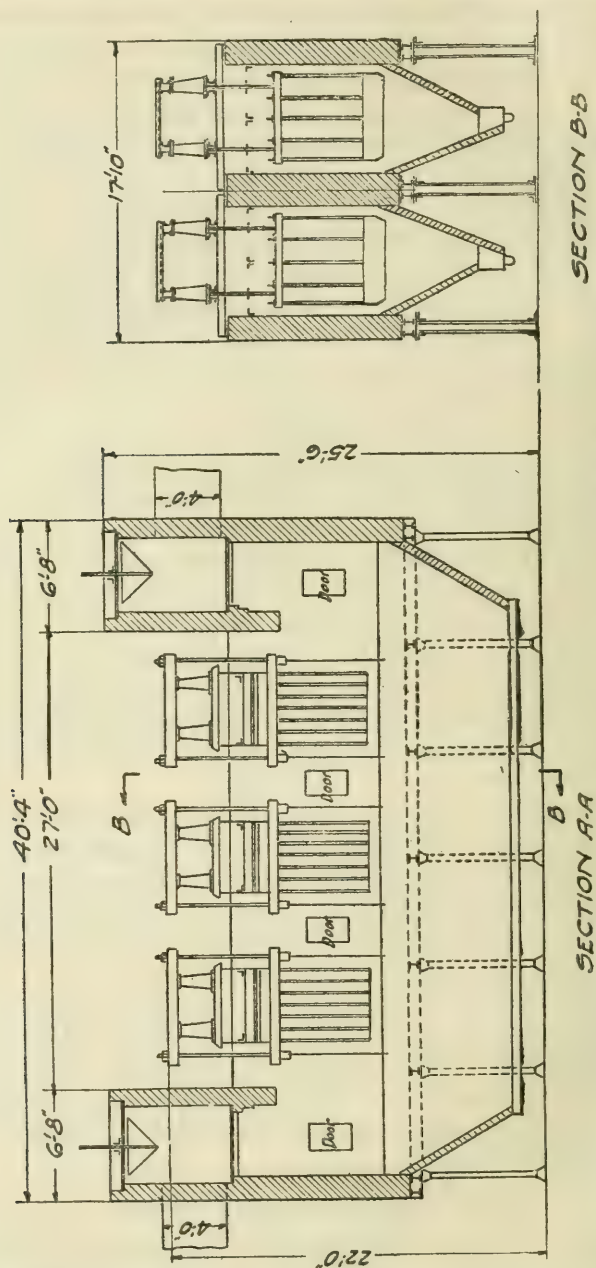
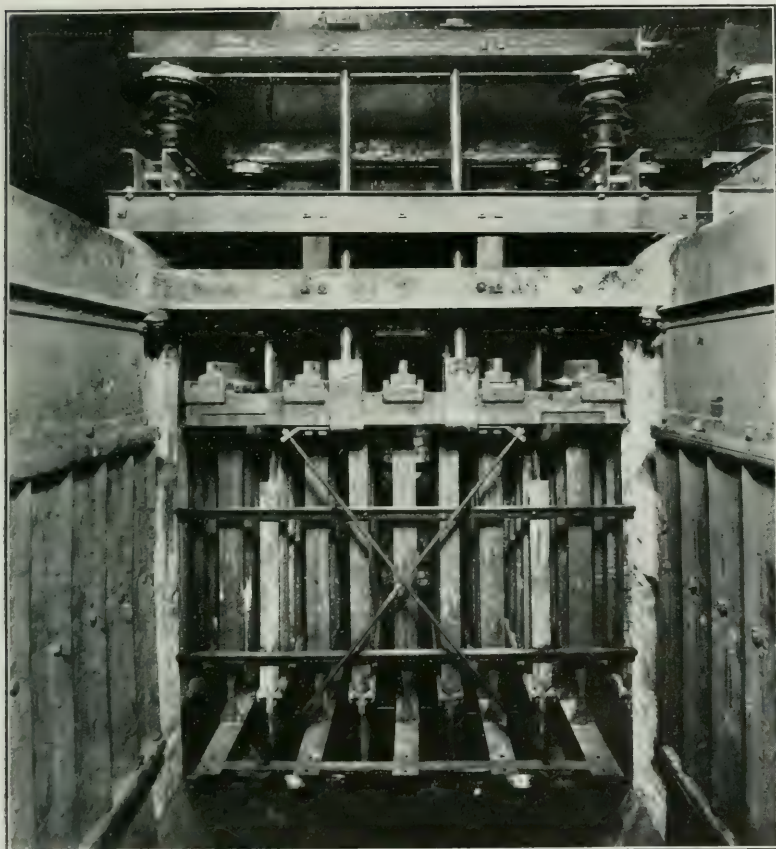


FIGURE 4.—General arrangement of electrical precipitation installation for cleaning gases from furnaces roasting pyrite fines. (By courtesy of the Research Corporation, New York.)

In the electrical precipitators the gases are caused to pass between two electrodes, one being grounded and the other under a high



INTERIOR OF ELECTRICAL PRECIPITATOR.

voltage, so that an electrical field of high intensity is maintained between them. In some plants the grounded electrodes are pipes through which the gases ascend or descend. In other installations the grounded electrodes are parallel plates of steel or sheet iron, the gases passing either horizontally or rising vertically between them. The charged electrodes are usually wires or chains or small rods. These electrodes are, of course, completely and carefully insulated. For charging this insulated electrode an intermittent direct current is used which is obtained by rectifying an alternating current of high potential. An alternating current from a power circuit is transformed to the desired high voltage, and the high-voltage current is then connected to the treater through a special rotary contact rectifier driven by a synchronous motor. The voltage employed depends upon the spacing of the electrodes and somewhat upon the nature of the gases and dust being treated. With a spacing of 3 inches between the charged and the grounded electrodes the difference of potential maintained is about 28,000 to 30,000 volts. As the gases pass between the electrodes the particles of dust and fume are electrified and are precipitated, mostly on the plate or pipe electrode. Means are provided for tapping both the charged and the collecting or grounded electrode in order to remove the dust adhering to them. Hoppers are placed beneath the treaters so that the collected dust may be removed readily.

No attempt will be made in this bulletin to discuss the theories of electrical precipitation, or the general application of electrical precipitation to the problem of removing dust and fume from metallurgical smoke. These points are described in various papers, chief among them being an article by Cottrell^a and one by Fulton.^b

Precipitators are designed in units with an excess total capacity so that one or more units may be shut off by dampers for repairs or cleaning without raising the velocity too high in the other units.

The treaters have usually been designed to treat the gases at a velocity of less than 10 feet per second, usually around 5 feet per second. Thus, to treat the gases from a furnace roasting 45 tons of pyrite a day and producing gas with a sulphur dioxide concentration of $7\frac{1}{2}$ per cent, or a total volume at 550° C. of about 13,000 cubic feet a minute, a treater having an effective area for passage of the gases of about 36 square feet would be necessary.

At the chamber acid plant of the Baugh Chemical Co., near Baltimore, Md., an electrical precipitator has been installed to treat the gases at a temperature of about 600° C., and occasionally, for short periods, as high as 750° C. At these high temperatures, certain

^a Cottrell, F. G., Problems in smoke, fume, and dust abatement: Annual report for 1913, Smithsonian Inst., pp. 653-685.

^b Fulton, C. H., Metallurgical smoke, Bu'l. 84, Bureau of Mines, 1915, pp. 59-65.

metallic fumes, such as arsenic compounds, would not be removed, but all dust and fume constituents possessing high volatilization points are effectively recovered.

At practically all acid plants where installed, the electrical precipitators have been satisfactory as dust collectors, and where the temperatures have been reduced to the necessary points, metallic fumes have also been recovered.

The Research Corporation owns and controls the right to the electrical precipitation process, as applied to cleaning gases from pyrite burners, throughout the United States, except in Washington, California, Idaho, Nevada, and Arizona. Either a royalty or a license fee is charged for the use of the process.

Some data relative to the electrical installations for cleaning furnace gases at acid plants in this country are given in the following table:

Data on electrical precipitator installations for cleaning roaster gases in the manufacture of sulphuric acid.

Installation.	Volume of gas, cubic feet per minute.	Temperature of gases, °F.	Type.	Source of gas.	Cost of installation.
A	15,000	1,200	Plate and strip, two sections.....	Pyrite—Herreshof burners...	\$18,000
B	8,650	1,000	Plate and strip, three sections.	Zinc ores—Matthiesson and Hegeler kilns.	20,000
C	12,000	600	Square pipe, 2 units of 20 pipes each	Zinc ores—Skinner kilns.	7,800
D	17,000	360	Pipe, 2 units of 36 pipes each.....	Zinc ores—Mathey kiln.....	39,000
E	8,000	1,300	Plate and strip, one section.....	Zinc ores—Matthiesson and Hegeler kilns.	12,500
F	18,000	800	Plate and strip, two sections.....	Pyrite—Herreshof burners...	24,000

From dust chambers or flues, or centrifugal separators, or electrical precipitators, the gases at a chamber plant are conducted directly to the Glover towers. At a contact plant the gases are conducted to scrubbing and cooling towers and through filters to remove the last traces of fume. These special fume removers are discussed later under the description of the contact process.

CHAMBER PROCESS FOR MANUFACTURE OF SULPHURIC ACID.

GENERAL PRINCIPLES.

The chamber process consists essentially in bringing together under suitable conditions sulphur dioxide, oxygen, and water, in the presence of the oxides of nitrogen, with the resultant formation of sulphuric acid. The reactions that actually take place between these substances in the chamber are rather obscure, although the end result is as though the reaction was $\text{SO}_2 + \text{O} + \text{H}_2\text{O} = \text{H}_2\text{SO}_4$ —that is, as though the oxides of nitrogen did not react. However, it is known

that this reaction will not take place in the chamber without the presence of the nitrogen oxides. In practice much more water is needed to bring about the reaction than is theoretically required for the production of H_2SO_4 . The sulphuric acid formed in chambers is therefore always dilute. The theory as to the chemistry of the reactions is discussed briefly below.

For the manufacture of sulphuric acid by the chamber process, besides the burners, flues, dust chambers, etc., there are three principal elements—(1) the Glover towers, (2) the acid chambers, and (3) the Gay-Lussac towers. In most plants the “niter pots” or retorts may also be considered one of the principal elements. In addition there must be the necessary fans, pumps, pipe lines, storage tanks, and other accessories. The general flow of gases and reacting material through these elements is as follows:

The gases coming from the pyrite or sulphur burners usually contain 5 to 8 per cent sulphur dioxide, a small proportion, usually less than 0.5 per cent, of sulphur trioxide, 10 to 14 per cent oxygen, about 80 per cent nitrogen, and some water vapor. The ratio of oxygen to sulphur dioxide depends on whether the material being burned is sulphur or pyrite. The dust is largely removed by the dust-collecting devices previously described; the hot gases then go to a Glover tower, passing upward through the packing or filling of the tower, where they come in contact with a down-flowing stream of weak sulphuric acid, and also the “nitrous vitriol” or the cold acid that has been used in the Gay-Lussac tower for recovery of the nitrogen oxides. Between the dust chamber and the Glover tower are usually placed the “niter pots,” in which the necessary quantities of oxides of nitrogen are generated and added to the gases going to the Glover tower to maintain the proper amount of those oxides in the system. Other methods of adding the fresh supply of nitric acid to the system will be described later.

The hot ascending gases evaporate a considerable portion of the water from the weak acid, thereby concentrating the sulphuric acid and at the same time releasing the nitrous acid from the “nitrous vitriol.” The released oxide of nitrogen, the sulphur dioxide gas, and the water vapor pass over into the lead chambers, where the reactions take place for the production of sulphuric acid. After leaving the chambers, the gases—consisting essentially of nitrogen, the excess oxygen, the oxides of nitrogen, and acid mist or water mist—are led through the Gay-Lussac towers, where the nitrous acid gas is absorbed and recovered from the waste gases by strong sulphuric acid, forming “nitrous vitriol.” The waste gases are discharged from the top of the Gay-Lussac tower either directly into the air or into a flue leading to a stack. As already indicated, the nitrous vitriol thus obtained is conducted to the Glover towers diluted with

chamber acid, and the nitrous acid gas is again liberated by heat and passed into the chamber system.

The acid produced in the chambers is dilute, containing only about 60 to 65 per cent H_2SO_4 , and at many plants a large part or all of this chamber acid is passed through the Glover tower and concentrated to about 75 or 80 per cent H_2SO_4 .

Although there are various types of chambers and intermediate towers and apparatus between chambers to increase the speed of the chemical reactions, the Glover towers and the Gay-Lussac towers are generally built on approximately the same lines and their operations are very similar at most plants.

Several theories have been advanced to explain the reactions occurring in the Glover towers and the lead chambers, and the part taken in these reactions by the nitrogen oxides. The most generally accepted theory is that of Lunge,^a which is a result of his elaborate investigations made in 1884. Under this theory, sulphur dioxide (SO_2), nitrous acid anhydride (N_2O_3), oxygen, and water vapor unite directly to form "nitrososulphuric acid," the reaction being as follows: $2\text{SO}_2 + \text{N}_2\text{O}_3 + \text{O}_2 + \text{H}_2\text{O} = 2\text{SO}_2(\text{OH})(\text{ONO})$. This complex compound floats around in the chamber as a mist until meeting water mist particles, either as water or in the form of very dilute sulphuric acid; the nitrososulphuric acid is broken up into sulphuric acid and nitrous acid, as follows: $2\text{SO}_2(\text{OH})(\text{ONO}) + \text{H}_2\text{O} = \text{H}_2\text{SO}_4 + \text{N}_2\text{O}_3$.

Various secondary reactions have been suggested. In the first lead chamber in the Glover tower where the temperatures are relatively high and there is an excess of water vapor, the following reaction is supposed to occur: $2\text{SO}_2(\text{OH})(\text{ONO}) + \text{SO}_2 + 2\text{H}_2\text{O} = 3\text{H}_2\text{SO}_4 + 2\text{NO}$. As there is usually an excess of oxygen also present the nitric oxide (NO) thus formed is at once brought into reaction again, as follows: $2\text{SO}_2 + 2\text{NO} + 3\text{O} + \text{H}_2\text{O} = 2\text{SO}_2(\text{OH})(\text{ONO})$.

If there is a deficiency of oxygen, the nitric oxide is not completely reoxidized to nitrous acid (N_2O_3) and returned to the process, but passes through the several chambers, and as the nitric oxide is not readily absorbed by the acid in the Gay-Lussac towers, it escapes into the atmosphere. A portion of the nitric oxide (NO) reacts with the sulphuric acid and oxygen or with sulphur dioxide, water vapor, and oxygen to form nitrososulphuric acid again; in other words, these reactions are reversible, and all of them may be taking place at the same time in the first chamber or in the Glover tower. Various other secondary reactions have been determined or their existence has been indicated, all of which are discussed in great detail in Lunge's book. It is to be noted that whatever may be the real se-

^a Lunge, George, Sulphuric acid and alkali, pt. 2, 1913, pp. 987-1038.

quence or types of reactions, in all instances the nitric acid and the oxides of nitrogen do not act as true catalyzers, inasmuch as these compounds themselves enter into the reactions.

The main reacting nitrogen compound or oxygen carrier is nitrogen trioxide, or nitrous acid anhydride, and the efforts discussed later to increase the efficiency of the chamber process have been largely aimed at increasing the activity of the nitrous acid.

THE GLOVER TOWER.

The chief functions of the Glover tower are: (1) The denitration of the nitrous vitriol, (2) the conversion into nitrous acid of the nitric acid which is added to make up for the nitrous acid lost in the process, (3) the concentration of weak chamber acid, (4) the cooling of the furnace gases, (5) production of acid in the upper part of the tower, (6) the cleaning of the furnace gases from impurities.

DENITRATION OF THE NITROUS VITRIOL.

The denitration of the nitrous vitriol is the most important and characteristic function of the Glover tower. The nitrous acid gas from the chambers is absorbed at the Gay-Lussac towers in cold sulphuric acid of about 78 per cent H_2SO_4 strength. The nitrous vitriol so obtained contains N_2O_3 in amounts equivalent to 2 to 4 per cent of NaNO_3 , or 30 to 60 ounces NaNO_3 per cubic foot of acid. This is diluted with weak chamber acid and is sprayed down over the packing of the Glover tower, where it is exposed to the ascending hot furnace gases. By the dilution and heat, together with the reaction with sulphur dioxide and water, the nitrous acid is released. To be properly denitrated, the strength of the acid entering the top of the tower should not be over 57°B . (72 per cent H_2SO_4).

The Glover tower top is designed to give a uniform distribution of the acid and to expose it in as fine a state as possible to the ascending gases. The acid feed to the tower should be carefully regulated, for not only is the chief quantity of niter supplied there, but also, by the concentration of the chamber acid, a large quantity of steam is generated for the chambers. In fact, the whole of the chamber reactions depend almost entirely upon the successful working of the Glover tower.

The denitration takes place in the upper part of the tower. The amount of sulphuric acid circulated through the Gay-Lussac and the Glover towers varies greatly at different plants, from a ratio of 1 ton of circulating acid to 1 ton of acid produced, to a ratio of 3 tons of circulating acid to 1 ton of acid produced. In common practice where

brimstone is used, and the plant is not being forced to work with low chamber space, the acid circulating is about 1.5 times the acid produced. With an average N_2O_3 content of the nitrososulphuric acid equivalent to about 2.5 per cent NaNO_3 , or 40 ounces NaNO_3 per cubic foot of acid, the NaNO_3 content of the nitrous vitriol is equivalent by weight to 13.8 per cent of the sulphur burned. In addition, approximately 3.5 per cent of nitrate of soda is added to the circulating acid, making the total proportion of NaNO_3 in circulation equivalent to 17.3 per cent by weight of the sulphur burned. When the chamber plants are being forced, that is, run at 11 cubic feet or less of chamber space per pound of sulphur, the amount of niter in circulation is usually nearly 30 per cent of the weight of the sulphur. No two acid plants shows uniform results as regards the content of oxides of nitrogen in the nitrous vitriol, or the volume of such acid being circulated per unit quantity of sulphur burned. A maximum figure for niter circulation should be decided upon for each set, as too much niter circulating has a detrimental effect upon the chamber leadwork. When pushing the chambers, and using a greatly reduced space per unit of sulphur burned, the niter circulation is necessarily raised and, as is shown in a subsequent connection, this undoubtedly contributes largely to the increased wear and tear found under these conditions.

The nitrous vitriol from the Gay-Lussac towers is usually diluted with weak chamber acid rather than water. The mixing is often done outside the tower, or the strong nitrous vitriol and the weak acid are fed separately into the top of the Glover tower through properly trapped holes and are then mixed in the top part of the Glover tower with, also, any nitric acid which may have been added to maintain the niter content. The dissolved nitrogen oxides are removed rapidly in the higher parts of the tower by dilution and heat and the presence of sulphur dioxide. The nitrososulphuric acid resists separation from the sulphuric acid, and the last traces of it are removed probably only by the following reaction: $2\text{SO}_2 (\text{OH}) (\text{O NO}) + \text{SO}_2 + 2\text{H}_2\text{O} = 3\text{H}_2\text{SO}_4 + 2\text{NO}$. The NO passing up the tower along with the oxygen is converted into N_2O_3 . Up to a strength of about 58°B. , sulphuric acid can be denitrated by hot sulphur dioxide gas, but it is not desirable to have the acid reach the zone of final denitration at a stronger strength than 58°B. , even though excess sulphur dioxide and water vapor may be present in that zone.

CONVERSION INTO NITROUS ACID OF THE NITRIC ACID ADDED.

For reasons that are discussed in a subsequent chapter (p. 118), there is always some loss of nitrous acid in the process, and this loss is usually made up by adding nitric acid.

Where the necessary nitric acid is added to the gases by "potting" the nitrate of soda prior to the entrance of the gases into the Glover tower, the Glover tower performs the function of converting the nitric acid gas into nitrous acid gas, through reactions with the nitrosulphuric acid, sulphuric acid, sulphur dioxide and the other oxides of nitrogen that are probably present, at least momentarily.

The most efficient, direct, and most easily controlled method of supplying the chamber process with the nitrogen oxides is to prepare outside the tower a mixture of nitric acid and sulphuric acid, and to add this nitric-sulphuric acid mixture with the nitrous vitriol from the Gay-Lussac tower. The nitric and sulphuric acid mixture is prepared by "potting" the nitrate and passing the nitric acid gases into sulphuric acid in a lead tank which is provided with cooling coils to keep the acid mixture cool and prevent loss of nitrogen oxides.

At some plants the bags in which the nitrate of soda is received are leached with water and the water solution of sodium nitrate is put directly into the Glover tower. Spent acids from explosives manufacturers, containing 10 to 15 per cent nitric acid and 70 to 80 per cent sulphuric acid, are occasionally introduced directly to the Glover tower, and the nitric acid is decomposed to nitrous acid and is taken into the system.

CONCENTRATION OF WEAK CHAMBER ACID.

As previously stated, in order to denitrate the nitrous vitriol it is necessary to dilute the vitriol, and this is usually done with chamber acid. The denitration takes place in the upper part of the Glover tower; the weak denitrated acid then descending through the tower is concentrated by the hot ascending gases, the resulting steam passing into the chambers to supply a part of the steam necessary for the process.

For towers of ordinary construction and in the customary practice, the Glover tower will readily concentrate to about 60° B. strength more acid than is required for the Gay-Lussac towers. In a well-designed tower and with hot furnace gases—that is, gases entering the tower at 350° C. or more—it is possible to concentrate all the chamber acid produced to 60° B., or even higher. The acid from the Glover tower issues hot, about 130° C., and usually contains a little sulphur dioxide, but is comparatively free from the oxides of nitrogen. This acid also contains arsenic and selenium if these metals were present in the ore, and dust or fumes either in solution or suspension if removal has not been effected in the dust and fume collectors.

COOLING THE FURNACE GASES.

If the hot furnace gases were permitted to enter the chambers without being properly cooled, the heat of the gases, when added to the heat of oxidation of the SO_2 to SO_3 , would be detrimental to the lead chambers and also to the process. Thus, just as it is usually important to conserve the heat in the gases going to the Glover tower in order to get the maximum evaporation possible, it is also desirable to reduce to a safe point the temperature of the gases as they issue from the Glover tower.

The temperature of the gases issuing from lump and fines burners will run between 450° and 600° C., and, as a satisfactory dust recovery can usually be obtained at less than 500° C., delivery of the gases to the bottom of the Glover tower at about 350° to 450° C. is possible. Gases from a brimstone burner can usually be delivered almost directly from the burner to the tower at a temperature around 450° C. The gases should issue from the top of the Glover tower at a temperature not higher than 90° C., otherwise cooling towers are necessary between the towers and the chambers. The usual temperature of the gases at the top is about 75° to 80° C.

PRODUCTION OF SULPHURIC ACID IN UPPER PART OF THE GLOVER TOWERS.

The liberation of the oxides of nitrogen in the Glover tower, in the presence of moisture and sulphur dioxide, together with the cooler temperatures at the top of the tower, gives the conditions requisite for the formation of sulphuric acid. In well-operated and well-designed towers as much as 20 per cent of the total production of acid from the plant may be formed in the tower. Usually the production in the Glover tower is only about 12 to 15 per cent of the total.

CLEANING THE FURNACE GASES.

As a rule, nearly all the very fine dust—oxide of iron, or unburned pyrite—that is mechanically carried through the flues and settling chambers by the gases is caught in the Glover tower, and is washed out of the tower by the acid either in suspension or as sulphate solution. With efficient dust collectors between the furnaces and the Glover tower, the quantity of this material collected in the tower should be relatively small. However, unless the gases are cooled and special devices are installed to collect the arsenic and selenium, the latter collect largely in the tower and are also washed out by the tower acid. Arsenic dissolves as arsenious oxide, and when present in large quantities sometimes separates again as fine crystals when the Glover-tower acid is cooled. When much arsenic is present, all of it is not

caught in the Glover tower, a large portion being carried on into the chambers, where it has a deleterious effect upon the lead. Selenium, when present, colors the acid red.

Zinc and lead fumes also are partly collected at the Glover tower when the ores being burned contain those metals.

CONSTRUCTION OF GLOVER TOWERS.

Nearly all Glover towers have an outer shell of lead, provided with an acid-proof stone, "volvic lava," or brick lining, and packed with pure massive quartz or acid-proof brick or tile. In plants recently constructed by the Chemical Construction Co. or the Process Construction Co. the lead shell has been eliminated and the towers are built entirely of chemical brick laid in an acid-proof cement.

The size and shape of Glover towers vary greatly. There are circular, square, rectangular, and octagonal shaped towers, varying in height from 15 to 60 feet and in area of external cross section from 25 to 700 square feet. It is claimed by many acid men that at an average plant the height of the tower should not exceed 25 feet, of which not more than 18 feet is filled with packing, and that the size should be a matter of variation in cross section rather than in height. The tower is designed to meet the demands made upon it, in any event being so proportioned as to absorb in concentration nearly all or all of the heat in the gases. Thus, the height and area should be determined largely by the nature of the raw materials to be burned, the possible heat loss between burner and tower, and the effective scrubbing surface afforded by the packing medium. While there is a tendency to build higher towers in order to utilize as far as possible the heat of the gases, and thus get good denitration and efficient concentration, yet unduly high towers tend to increase condensation in the upper part, and thus the net result is to reduce the effectiveness of the tower as a concentrator.

As to the shape of the tower, some constructors prefer one form, some another. For a unit weight of lead, acid-proof brick wall, and tower lining the circular tower has a greater surface area for scrubbing or absorption than the square or rectangular tower, and there are no dead corners, etc. With proper gas and acid distribution, the efficiency of the towers of different shapes per unit of packed volume does not vary greatly. For lining round towers special radial brick are required, and these are more expensive to make and to lay than the square brick. A tower of square, rectangular, or even octagonal section is much easier to construct than a round tower, especially if the tower is to be built of acid-proof brick.

In designing a Glover tower it is necessary to provide for the severe duty the tower is called upon to perform. Part of the tower

is in contact both with gases having a temperature ranging up to possibly 500° C. and with sulphuric acid having a strength ranging up to 60° B. or even 66° B. In other parts of the tower are present nitrogen oxides, sulphur dioxide, sulphuric acid, and steam. Thus, if chemical brick or tile are used for lining or for packing, they must be of the best selected quality.

When lead is used for the tower outer walls, as has been the usual construction, it is customary to make the top and sides of 16-pound lead and the bottom of even heavier lead. The tower should be built on a firm masonry foundation which is covered with a thin layer of pitch and sulphur melted together and further protected by the acid pan of lead. Some designers attempt to cool the under-side of the tower bottom by introducing air channels or by having water circulate around the pan.

The framework for the towers may be of wood or steel. Wooden frames are still common, though steel is usually preferred, especially when the towers are built of acid-proof brick.

It is customary to provide a fairly thick lining to conserve the heat. In the lead towers the usual method is to make the lining at the bottom 18 inches to 24 inches thick up to a point above the top of the gas inlet. Above this point the thickness is then reduced, leaving a shelf 6 inches to 9 inches wide, which extends around the tower. Resting partly upon this shelf and partly upon several piers or arched walls, which are carried up to the same height, is the grid that supports the tower packing. Below this "grid" or "grill" is a chamber of considerable size, the walls or piers supporting the grid being so arranged that their presence does not obstruct the passage of the gases but tend to distribute the gases evenly over the entire bottom of the tower.

The grid may be of deep, narrow beams of "volvic lava" or of acid-proof stoneware. The spaces between the ends of the grid beams should then be filled with lining brick to prevent the beams from falling over sidewise.

The repacking of a Glover tower is an expensive operation and great care should be exercised in the selection of the material going into the tower and also in the manner of placing the grid and the tower packing.

Various methods have been employed for packing towers, and it is not thought desirable in this paper to discuss the methods in any detail. Unless the design and construction of a tower can be based upon satisfactory actual experience, it is best to employ an expert to lay out the tower. This remark, of course, also applies to the design and construction of the whole acid plant. A tower too tightly packed offers too great a resistance to the passage of the gases, which causes the gases to travel through the spaces at too high a velocity

and also results in an unduly high cost of power for pulling or driving the gases through it. A tower too loosely packed is as objectionable as one too tightly packed, for although the velocity of the gases is reduced, the descent of the acid is accelerated and the necessary length of time for the reactions, etc., is not given.

For the packing material, flint or massive quartz formerly were used exclusively. The quartz to be entirely satisfactory must be free from cleavage lines and contain no admixture of schists or foreign matter. Acid-proof brick is now being made which lasts almost indefinitely, except where the ore, which is burned to produce the acid, contains fluorite. The hydrofluoric acid or fluorine produced decomposes the brick. One instance is recorded where the Glover tower packing was rendered valueless within two years by the presence of fluorite in the ore used. Frequently the towers are packed partly with chemical brick and partly with quartz—say the lower three-fourths of brick and the upper one-fourth of quartz.

A typical modern Glover tower is that designed by the Process Engineering Co. and built by the Calumet & Arizona Mining Co., at Douglas, Ariz. The chamber plant has a capacity of 210 tons of 60° B. acid per day. The Glover tower (fig. 4) is octagonal, 22 feet 2 inches in diameter by 56 feet high. It has a steel frame holding the walls, which are built of duro brick laid in "duro" cement, containing about 96 per cent silica mixed with sodium silicate as a binder. The tower is packed with duro tile, 1½ by 6 by 12 inches, laid in checker formation. The tiles are so laid as to be self-supporting and thus exert no thrust upon the walls, as when quartz packing is employed. This acid resistant "duro tile" is made by the Harbison Walker Refractories Co.

Another modern form of Glover tower packing is the "chemico" ring, made by the B. Mifflin Hood Brick Co., of Atlanta, Ga., under a license by the Chemical Construction Co. These rings are made in 3-inch and 6-inch sizes. The ring (see Pl. II, *B*, p. 61) contains in the interior a ribbon-like spiral winding from top to bottom, all made in one piece of chemical stoneware.

With a tower 25 feet high the actual packing will not exceed 16 feet in height—12 feet of checkered brickwork and 4 feet of quartz. If brick is used, the brick should be placed on edge, forming spaces say 4 by 4 inches. The actual packing space usually allowed per ton of sulphur burned daily is 200 to 300 cubic feet.

The top of the tower is of lead, or in the towers constructed of acid-proof brick the tops also are of brick. The top plate is not so subject to heavy wear and tear because it is largely cooled by the incoming acids, and, being somewhat above the outlet from the tower, is at the top of a dead space.

Various schemes are in use for distributing the nitrous vitrol or weak chamber acid through the top of the Glover tower onto the packing. The most common is to provide small depressions or cups

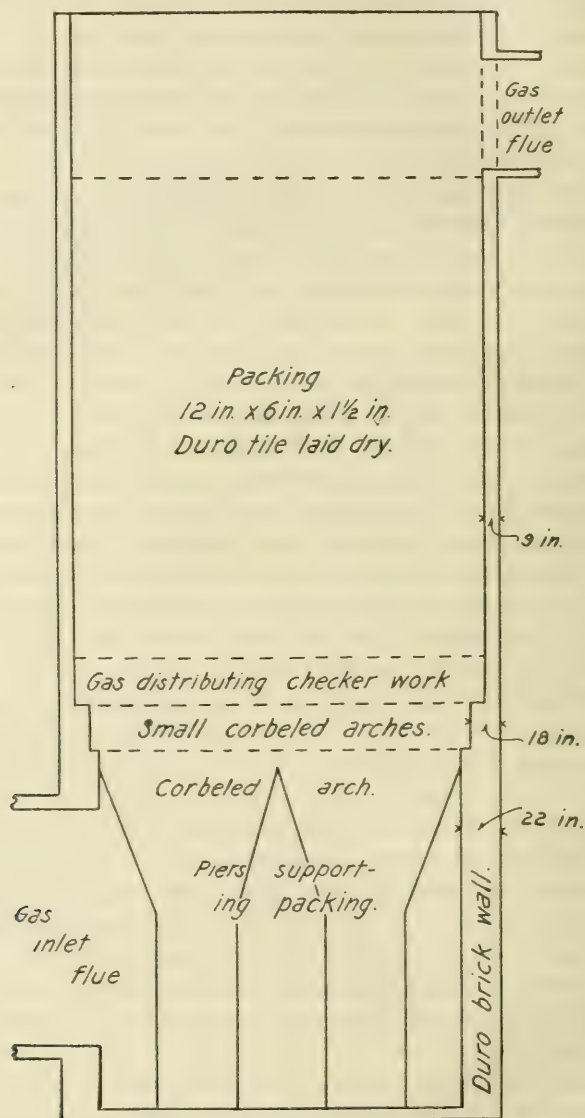
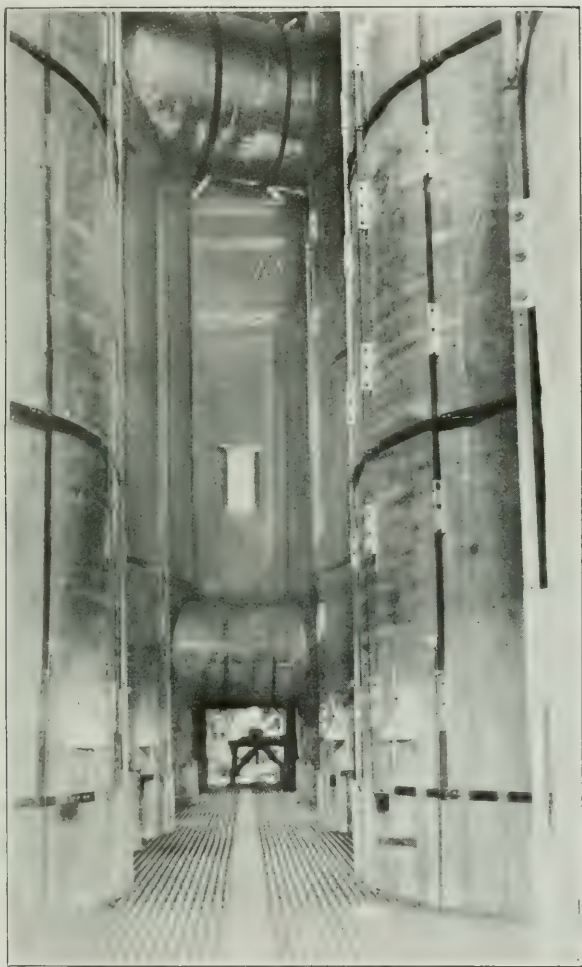


FIGURE 5.—Outline sketch of Glover tower. (By courtesy of Mining and Scientific Press.)

all over the top, each cup being oval and divided by a partition into two equal acid-receiving cups. At the bottom of each of these half cups a small pipe extends down into the tower a few inches, and up into the half cup 2 to 5 inches. Lead thimbles inverted over the



COOLING TOWERS AT PLANT OF CALUMET & ARIZONA MINING CO.

(By courtesy of the Mining and Scientific Press.)

upstanding pipes complete the liquid lutes. As the acid runs from distributing pipes into the depression it fills the depression until it overflows down the upstanding pipe into the tower.

In many plants lead pipes emanate from a trough or series of troughs placed on top of the tower, and the acid is carried directly by these pipes through the top and falls on the tower packing.

COOLING TOWERS BETWEEN GLOVER TOWERS AND CHAMBERS.

At plants equipped with low Glover towers, or where the temperature of the gases going to the tower is so high that the gases issue hot from the top of the tower, it is necessary to cool the gases before they are admitted to the chambers. Cooling towers vary widely in size and shape, material used, and other features. The cooling towers (Pl. VI) designed and constructed by the Process Engineering Co. at the plant of the Calumet & Arizona Mining Co., may be mentioned as satisfactory modern coolers. The towers are 41 feet high and $17\frac{1}{2}$ feet in diameter and are built of lead sustained by a steel frame. The gas enters at the bottom and leaves at the top, both inflow and outflow pipes being connected tangentially so as to induce a spiral motion to the gases. It is claimed that this motion drives the gases toward the periphery, and facilitates radiation of heat through the lead walls.

CHAMBERS.

The gases leaving the Glover towers or cooling towers consists principally of sulphur dioxide, with a large percentage of sulphur trioxide, nitrous oxide, oxygen, nitrogen, and water vapor. Usually, if the Glover tower has been functioning properly, the gas contains sufficient water vapor to carry on the process for a considerable distance in the chambers. The functions of the chambers are:

(1) To afford space in which the gases may mix and the various chemical reactions take place by which sulphur dioxide is converted into dilute sulphuric acid. These reactions have been discussed in a preceding paragraph.

(2) To radiate the heat produced by the chemical reactions.

(3) To afford surfaces to facilitate condensation of the sulphuric acid as it is formed.

In carrying out these functions of the chamber, it is necessary to add water vapor in addition to that present in the gases coming from the Glover tower.

The efficiency of a lead chamber plant is measured by (1) the amount of chamber space required for each unit of sulphur burned per unit of time, usually expressed as cubic feet of space per pound

of sulphur per 24 hours, (2) the amount of acid made per unit of sulphur burned, and (3) the consumption of nitrate of soda.

It is generally agreed that, provided the gases are present in the proper proportions, the two most important conditions necessary for efficient production are (1) thorough mixing of the gases and (2) perfect control of temperature.

The necessity of thorough mixing of the gases is evident, as intimate contact of the reacting substances with each other is essential for complete reactions. In making acid too low a temperature lessens the activity of the gases, whereas a temperature above 100° C. prevents the condensation of water necessary for the completion of the reactions.

In earlier days the chamber space consisted of a single long horizontal chamber, and the reactions were all completed in this chamber. The space required for the completion of the reactions in the single-chamber system, however, was excessive, and gradually series of smaller chambers were substituted.

As the sizes of the plants were gradually increased and the number of chambers at a plant was increased considerable attention was given to the subdivision of the total chamber space in such a way as to increase its efficiency. F. J. Falding, one of the leading experts in acid manufacture during the period of rapid growth of the industry in the South, advocates that if the cubic capacity of the plant is large, the proper method of design was to proportion that space between, say, three or more chambers, having the proportion between chambers 1, 2, and 3 as 4:2:1. Falding also advocated chambers of exceptional height, which type of chambers will be discussed later.

In modern construction of the ordinary horizontal type of chamber plant it is customary to build the chambers of a plant with approximately equal capacity, even when the plant is very large. The height is rarely more than 40 feet or the width more than 60 feet, but the length may vary from 50 to 236 feet. The latest chambers of the Tennessee Copper Co. are 236 feet long. In any given set of ordinary horizontal chambers it is rarely advisable to vary the sectional area, and this seldom can be done with saving of ground space, labor, or building economy. The sectional area employed is usually determined by the structural and economic conditions at the plants. In general, the cheapest sectional area, other factors being the same, is that which will give the least area of lead surface with the greatest cubic capacity. However, as the smaller lead surface area reduces the radiating capacity of the chambers, the saving in chamber construction may be offset by the necessity of providing extra cooling towers between chambers. Recent data collected from a number of plants having the ordinary horizontal rectangular chambers in different sizes, from 15 to 45 feet in height, from 20 to 60 feet in width,

and from 50 to 230 feet long, showed a variation from 8.5 to 20 cubic feet in the chamber space required per pound of sulphur burned per day. Most plants that were seemingly operated with fair efficiency, and were burning high-sulphur pyrite or brimstone, were using 11 to 13 cubic feet of chamber space. A few plants were using less than 10 cubic feet, and several especially well operated plants using brimstone were using less than 9 cubic feet of chamber space. Many plants treating waste gases at zinc or copper plants were so handicapped by the fluctuations in gas concentration and by the average low concentrations that a much greater chamber space was required. At zinc plants during the war much higher chamber efficiencies were obtained by burning brimstone in conjunction with the zinc ore, so that the gas concentrations were higher and the percentage fluctuations much less.

With the ordinary type of plant, the yield of sulphuric acid is usually about 4.65 tons of 50° B. acid per ton of sulphur burned, as against a theoretical yield of 4.92 tons per ton of sulphur burned. Thus, the ordinary type of chamber plant has an average efficiency of about 94.6 per cent. Some of the ordinary plants, however, have made for long periods as much as 4.8 tons 52° B. acid per ton of sulphur burned or 97.6 per cent of the production theoretically possible.

Practically all the active work of an ordinary horizontal chamber is performed within the first 30 per cent of its chamber space. The remainder of the chamber is relatively much less efficient unless special means are employed to mix the gases vigorously and permit condensation of the vapors or mist.

There have been many modifications of the ordinary type of chamber plant, involving changes in the design of the chambers and also changes outside the chambers in the form of cooling towers, "converters," intensifiers, and other apparatus, all designed to provide more efficient cooling and mixing of the gases. Before passing to a description of these, however, it will be well to discuss a few of the more important features involved in the operation of the ordinary chambers, as many of these considerations are applicable to all types of chamber plants.

IMPORTANT FEATURES OF OPERATION.

ADDITION OF WATER.

The water vapor coming over with the gases to the chambers from the Glover tower is usually sufficient to carry on the process in the first part of the chamber. From then on, more water vapor must be added to maintain the process. Formerly, the supply of water vapor

to the chambers was almost universally in the form of steam at low pressure, the steam being admitted through the roof of the chambers. In some more recent installations, the water is added to the front chambers as spray and to the rear chambers as steam. Some plants use only water. In a plant of recent construction, where there are six chambers, each 143 feet long, 59 feet wide, and 41 feet high, with cooling towers between the chambers, the total capacity of the chambers and intermediate cooling towers being about 2,155,000 cubic feet, the water is added through Schutte & Koerting platinum-tipped sprays as a very fine mist. The first chamber of this installation is provided with 12 jets, each spraying $2\frac{1}{2}$ gallons per hour; the second chamber has 24, the third has 28, and the fourth has 24 jets, each of these spraying 5 gallons per hour; the fifth has 20, and the sixth has 12 jets, each delivering $2\frac{1}{2}$ gallons per hour. The intermediate cooling towers also have one jet each, spraying $2\frac{1}{2}$ gallons per hour.

At the large chamber plant of the Tennessee Copper Co., where an enormous number of low-capacity sprayers would have been required to supply the quantity of water needed for the large-scale operations, a special atomizer has been developed which is capable of atomizing as much as 50 gallons of water per hour. By the use of this atomizer, water spray has been substituted for steam in most of the chambers. A new spray (U. S. patent No. 1099028), manufactured by the Monarch Manufacturing Works, Philadelphia, Pa., is now on the market.

The advantage of water sprays over steam lies principally in a saving of coal and lower temperatures in the chambers, which results in a considerable saving in chamber space.

The water used in the sprays must be well filtered in a general filter, and in addition a small lead strainer provided with the finest mesh wire gauze should be inserted in the water-supply line next to the spray nozzle.

For a given charge of sulphur producing a constant supply of gas of uniform sulphur dioxide content, with a Glover tower supplied with a steady stream of nitrous vitriol and nitric acid, a constant supply of water vapor to the chambers will be required. Therefore, after the steam or water supply is once regulated and means are taken to insure its admission at a uniform rate, no change should be required until something goes wrong, when the cause for the change must be determined and rectified.

STRENGTH OF ACID DRIPS.

The addition of water vapor is generally governed by the strength of the acid in the "drip cup" (fig. 6). Usually the drip cup is a

small trough or saucer, *a*, burnt on the inner surface of the lead curtain or side wall of the chamber, and communicating with the outside by a pipe, *b*, bent to make a seal. This trough collects the acid as it drips down on the surface of the lead above the cup; the acid thus collected drains through the seal into a small jar, *c*, provided with a hydrometer. Table drips are also occasionally used, consisting of lead pans set well within the chamber and away from the side and connected by means of a lead pipe with the exterior of the chamber, similarly to curtain drips.

The acid collected by the curtain drips is usually 3° or 5° B. weaker than that collected in the table drips. The lead walls, owing to the radiation of heat from them, are cooler than the interior of the chamber, and therefore more water condenses there than in the interior, thus making the acid at the walls weaker than in the interior.

The strength of the acid in the drips varies considerably at different plants, and the relation of the strength in the drips to the strength of the acid actually falling over the chamber bottom should be known at each plant and at each chamber. It is evident that the absolute strength of the drip is not so important as is the variation of strength from day to day and from the first chamber to the last. A curtain-drip strength of, say, 50° B. means nothing unless from experience and frequent tests it is known that this reading at this special drip or set of drips shows that the acid formed in the chamber in question has a certain relative strength. Furthermore, as will be shown later, drip strengths are of little value as an indicator of operations unless taken in conjunction with chamber-temperature readings.

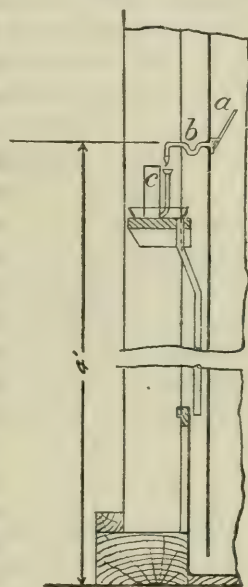


FIGURE 6.—Chamber drip. *a*, saucer; *b*, connecting pipe; *c*, receiver.

Within certain limits the strength of the drips may vary without any serious consequences. In the first chamber, or rather in the front part of the first chamber, where the water content of the mixture is dependent largely upon the steam generated in the Glover towers, the acid strength can not be controlled closely, but the strength seldom falls below 52° B. If there is a deficiency of water in the chambers, and the strength of the sulphuric acid being formed gets much above 52° B., the sulphuric acid begins to absorb nitrous acid in considerable quantities. The conditions for the formation of sulphuric acid in the reactions between nitrososulphuric acid and water are deteriorated; thus with deficient moisture, and especially

if the temperature falls too low, the nitrososulphuric acid may separate as crystals, which deposit at various points on the walls as "chamber crystal." When steam or water comes in contact with the crystallized nitrososulphuric acid it decomposes into sulphuric acid, nitric oxide, and nitrogen peroxide (N_2O_4) according to the equation $4\text{SO}_2(\text{O H})(\text{O NO}) + 2\text{H}_2\text{O} = 4\text{H}_2\text{SO}_4 + \text{N}_2\text{O}_4 + 2\text{NO}$. The N_2O_4 unites with H_2O to form nitrous acid (HNO_2) and nitric acid (HNO_3) directly on the walls, corroding the lead at the point where the crystals were attached.

If too much water is present and the acid becomes sufficiently weak to permit the formation of nitric acid in the chambers (by the reaction $2\text{NO} + 3\text{O} + \text{N}_2\text{O} = 2\text{HNO}_3$; or $\text{N}_2\text{O}_3 + 2\text{O} + \text{H}_2\text{O} = 2\text{HNO}_3$) there results a loss of niter into the chamber acid and also serious corrosion of the lead walls of the chamber. This conditions is shown by the paling of the color of the gases in the chamber.

A rough indication as to the moisture condition in the chamber is obtained by the appearance of bell jars covering small openings in the chamber. A white crystalline covering of "chamber crystal" which turns green when moistened indicates a deficiency of moisture. Dripping moisture on the glass jars indicates too much water.

The acid formed in the chambers should not be weaker than 45° B. and should not be stronger than 54° or 55° B. In common practice the strength is usually about 52° to 54° B. The strength of acid in the back chambers is somewhat less than in the first, but even in the last chamber should not be less than 45° B.

TEMPERATURE CONTROL.

The reactions taking place in the chamber generate large quantities of heat, and this affects the temperature of the gases in the chamber more than any other factor. As a general rule the more rapidly the heat is carried away the better both for the process and for preventing corrosion of the lead. In the ordinary horizontal chambers whatever cooling is done is by radiation from the surface of the lead, unless cooling towers are interposed between the chambers. Cooling is very important and the proper relation between the cooling surface and the chamber capacity should be maintained. As a rule, every effort is made to facilitate radiation from the chambers. All chances for air to circulate around the chambers are usually given, and the outside of the lead is kept free from nonconducting surfaces. Many devices have been employed, some of which are described elsewhere in this paper, to dissipate the heat rapidly and thus also to increase the rapidity of the condensation of sulphuric acid mist.

The temperature of the gases in a chamber is a sensitive and reliable index of the activity of the process going on in the chamber.

A slight variation, even less than 3° C., in the temperature difference between two points in the chamber at some distance apart indicates a change of conditions which may lead to trouble, such as a variation in the sulphur dioxide concentration, a variation in the strength or quantity of the fresh niter supply, or nitrous vitriol, to the Glover towers, or fluctuation in the pressure of the steam or in the quantity of water being used. If the chambers are supplied with a gas containing a constant percentage of sulphur dioxide, nitrous oxides, and a sufficient and constant supply of steam or water, the process will remain constant and regular, as will be shown by the drips, color of the gas, and more than by any other way, by the temperature readings in each chamber. The gases usually enter the first chamber at about 90° C. and grow cooler as they pass through the succeeding chambers, leaving the last chamber at a temperature of not more than 30° to 45° C., according to the outside temperature. The temperature of every chamber diminishes from front to back, and, as stated above, the difference in the normal process ought to be constant.

NITER SUPPLY.

The percentage of niter or nitrogen oxides in the gases has great influence on the temperature without necessarily affecting the yield of acid or the consumption of niter. The simplest indication of niter conditions is the color of the gases. Thus, sight holes are provided at convenient heights in the chamber walls and in the exit pipe from the last chamber for observing the color of the gases. In the first part of the process the presence of a relatively large proportion of sulphuric acid mist prevents any color being observed. In fact, the presence of sulphur dioxide prevents the formation in any important amount of oxides of nitrogen other than the nitric oxides. As the gases progress through the chambers, the amount of reacting sulphur dioxide, and therefore of sulphuric acid mist, decreases, the greater proportion of the higher nitrogen oxides begins to color the gases a more or less reddish yellow. Before the gases pass from the chambers into the Gay-Lussac tower the red oxide (N_2O_4) is present in sufficient proportion to give a dark reddish color to the gases.

The supply of niter to the process—that is, the amount of nitrous acid in the chambers—may vary considerably without serious results. However, there are limits, both in regard to an over supply as well as to an inadequate supply. If too much niter is supplied the temperature rises too much, the chamber lead is acted upon and there is usually an unduly high loss through the Gay-Lussac towers. An excess of niter is evidenced by the chamber gases being too dark,

by the presence of much nitrous acid in the chamber acid, and by the presence of nitric acid in the Gay-Lussac tower acid.

A deficiency of niter is more objectionable than an excess, by slowing down the reactions, causing a loss of sulphur dioxide and consequent decrease in production. This condition also causes loss of nitric oxide and nitrous oxide to the Gay-Lussac towers where these are not recovered. The result is an unduly large loss of niter from the system, to which is also added the loss of niter from the decomposition of nitrous vitriol in the Gay-Lussac tower by the sulphur dioxide. The deficiency is indicated by the paleness of the gases at the end of the chamber, the decreasing strength of the Gay-Lussac tower acid, and by a decrease in quantity or strength of drips. Red fumes of N_2O_4 in the Gay-Lussac stack, due to the decomposition of nitrous vitriol by the sulphur dioxide, may also indicate a deficiency of niter.

A method commonly employed for determining the niter conditions in the chambers is by determining the nitrosity of the chamber acid. An accurate quantitative determination of the nitrogen oxides and nitric acid can not be made readily, but a simple and quickly made colorimetric test with ferrous sulphate is satisfactory for the purpose. Briefly described, the method is as follows: A sample of drip or chamber acid is obtained in a test tube and a solution of ferrous sulphate is poured in carefully so that the liquids are not mixed. If traces of the higher nitrogen oxides are present, a yellow ring is formed at the point of contact. The ring is darker and darker as the proportion of nitrogen oxides is greater until it becomes a deep brown or black. By practice and experience it is possible to get a fair idea of the niter conditions in the chamber by this test, in connection with the color of the chamber gas as observed through the windows.

As the nitrate of soda is the largest single item of expense in operating a chamber plant, much effort is directed toward the conservation and recovery of the nitrogen oxides. To this end the Gay-Lussac towers are used. However, even with the best types and method of operation of the Gay-Lussac towers for the recovery of these oxides, the efficiency of the towers largely depends upon the proper regulation of the water supply to the chambers, upon the efficient cooling of the gases in the chambers, and upon the careful introduction of just enough niter for the oxidation of the sulphur dioxide admitted to the chambers.

When the loss of niter is supplied by the Glover towers and by adding nitric acid or a prepared nitro-sulphuric acid mixture, such careful introduction of the amount of niter is possible. When the niter is supplied by the more or less intermittent method of "potting" the nitrate, there will be intermittent advance and retreat of

the active zones of chemical action. In most plants, unless the niter feed varies widely, the chamber system is usually large enough to compensate for these variations and prevent the entry of sulphur dioxide into the Gay-Lussac tower.

CONTROL METHODS USED WHERE GASES ARE OF VARIABLE COMPOSITION.

As previously stated, the well-known and routine methods of controlling the process are based upon (1) observing the strength of the acid in the drips and the comparative nitrosity of the acid; (2) observing the difference in temperature at different parts of the chamber system and learning by experience what differences will yield the best results and bring about the best recoveries of nitrogen oxides in the Gay-Lussac tower, and (3) by observing the color of the gases in the chambers, or connecting flues, by means of "windows" or sights. These methods are satisfactory as long as the gases entering the Glover tower contain a substantially uniform percentage of sulphur dioxide. When the gas concentration is liable to vary widely, as in plants manufacturing acid as a by-product of zinc or copper smelting operations, this method of control is hardly adequate to yield the most economical results.

The Fairlie method of controlling the chamber process (U. S. patents 1205723 and 1205724) involves the establishment, as a result of experiment, of a series of desirable ratios between the percentage of sulphur dioxide in the gas entering the Glover tower and the percentage of sulphur dioxide in the front chamber, covering the entire range of sulphur dioxide percentages that are likely to be encountered, and in maintaining thereafter such desirable ratios constantly by introducing the right amount of nitrate of soda into the system. Once determined, the desirable ratios are arranged in a tabular form, the table being posted in a convenient place for reference by the chamber operator. An increase in the sulphur dioxide ratio above that desirable indicates the need of more niter, whereas a decrease below the desirable ratio indicates that the quantity of niter must be reduced. This method has been in use daily at the large acid plant of the Tennessee Copper Co., which has been operating on gases from copper blast furnaces.

Once the regularity of operation in the chamber is so greatly upset that the Gay-Lussac towers are not functioning properly, a certain loss of niter and sulphur dioxide is practically inevitable. The best method of correcting the trouble is to add sufficient niter in the Glover tower to make up for the decreased niter in the Gay-Lussac tower acid, in order to get things going normally again at the front of the chamber system. Gradually the normal condition will be re-

sumed throughout the entire system and the Gay-Lussac towers will absorb the nitrous acid properly, by which time the whole plant will be back to a normal basis of operation.

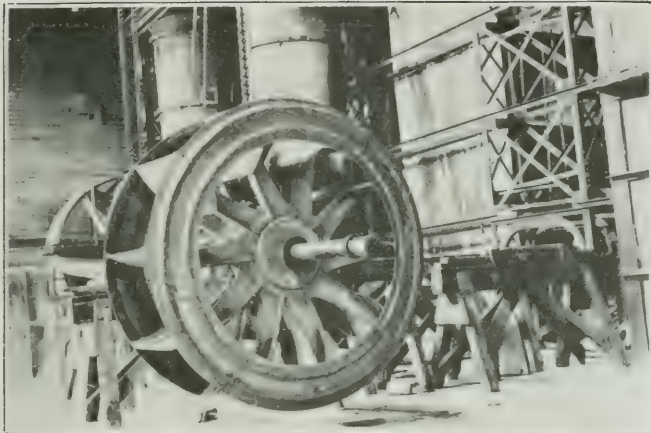
In order to increase the rate of reaction in the chambers and thus decrease the chamber space required, the "intensive" system has been tried. This system involves increasing the proportion of nitrogen oxides to that of sulphur dioxide in circulation and thereby accelerating the speed of the initial reactions. Intensive or high-pressure working leads to higher costs than a normal rate of production, owing partly to the comparatively great wear and tear on the chambers, and the increased consumption of nitric acid, hence can not be carried beyond a certain economic point. During the war many plants in this country used this method to increase the capacity of the plants. Plants ordinarily operating with a chamber capacity of 12 to 13 cubic feet per pound of sulphur treated daily and a niter consumption of 3.5 to 4 per cent, increased the production by decreasing the chamber space to 9 or 10 cubic feet per pound of sulphur, but at the same time at plants where the Gay-Lussac tower capacity was not adequate for the increased volume the niter loss was increased to more than 4.5 or 5 per cent. In some plants the wear and tear on the chambers was evidently increased, but in others, where sufficient cooling surfaces were present, the increase in depreciation was negligible.

The division of the initial volume of gases to two or more leading chambers in parallel instead of in series with a considerable reduction of the secondary chamber space, has been efficacious in reducing to some extent the total chamber space required. Such subdivision of the gas can be obtained easily or positively by the use of fans.

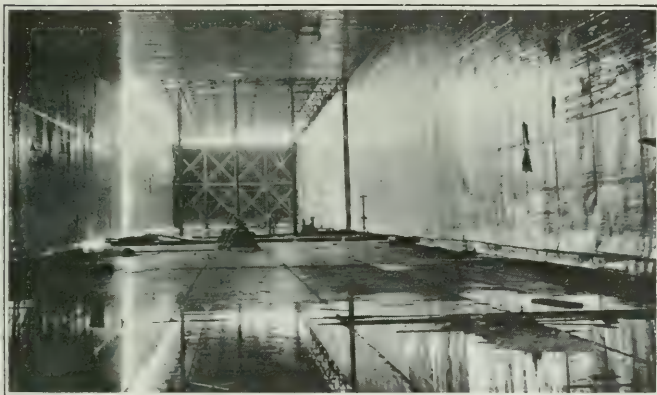
FURNACE DRAFT.

Nothing has yet been said in regard to the draft on the system and the means of moving the gases through the chambers and other apparatus. In an ordinary small plant where there is no fan employed to create the draft, the draft on the furnaces is produced (1) by the slight vacuum caused in the chambers and other condensing apparatus by the condensation of sulphur dioxide into sulphuric acid and by the contraction due to cooling of the gases, (2) by the tendency of hot gases to ascend, and (3) by the chimney, stack, or inspirator placed at the exit of the system.

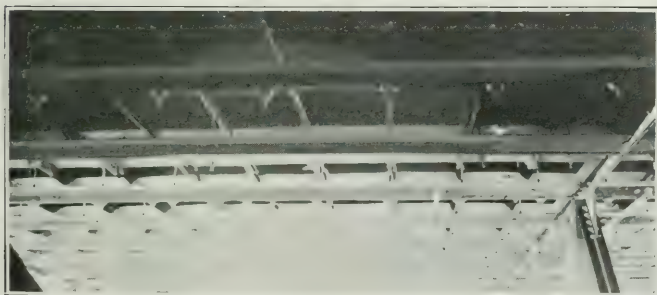
However, the working of a plant on natural draft is not satisfactory, especially for a large plant, as this form of draft is dependent largely upon the regular operation of the plant and is seriously affected by adverse and changeable meteorological conditions.



A. FAN FOR DISCHARGING GASES THROUGH LEAD CHAMBER.



B. INTERIOR OF LEAD CHAMBER.



C. METHOD OF HANGING TOP SHEETS OF LEAD CHAMBER.

(By courtesy of the Mining and Scientific Press.)

In many plants a satisfactory and positive draft is maintained by a fan placed at the end of the chamber system to draw the gases through the entire system, even including the burners, and discharge them through the Gay-Lussac towers. This arrangement is feasible at a plant burning brimstone and where there are few or no intermediate towers. With many intermediate towers, or with a closely-packed Glover tower, the draft necessary to overcome the resistance caused by these towers would be so great that the chamber walls might be seriously collapsed. Therefore, in modern plants there is usually a fan between the burner and the Glover tower or between the Glover tower and the chambers, or the cooling towers before the chambers, to draw the gases from the burners through the Glover tower and to discharge them through the chambers. The fans used for this work are lead lined and have hard lead (antimonial lead) impellers. The vanes of the impellers (Pl. VII, A) are attached to the hub by cast-lead arms. Keyed to the cast-lead hub there is an inner hub of cast iron and to this is keyed the steel shaft. Some plants are provided with fans both before and after the chambers.

Modern installations permit adjustment of the speed of the fan within fairly wide limits and thus afford control of the draft on the furnaces to give the desired gas concentration, etc. As stated previously, the gases from a pyrite burner under good technical control will contain about 7.5 per cent sulphur dioxide and about 9 per cent oxygen, the rest being nitrogen and water vapor; the gases from a brimstone burner will usually have a sulphur dioxide content of 8.0 to 8.5 per cent. Such a gas mixture will contain sufficient oxygen to oxidize the sulphur dioxide to sulphur trioxide and also provide the necessary excess of 5 per cent oxygen for satisfactorily working the chambers.

CHAMBER CONSTRUCTION.

As in the last 10 years several construction companies in this country have made a specialty of chamber-plant construction and have developed special types suitable for different conditions and localities. it is not necessary in a paper of this character to discuss the construction of the chambers beyond outlining briefly some of the fundamental principles that underlie all chamber construction.

Chambers should always be placed at some elevation above ground level so that the bottoms are accessible for cooling and for observation to ascertain whether the chambers are tight. The chambers must therefore be supported by pillars, usually of brick or cast iron, or, in small plants, of wood.

The framework supporting and surrounding the lead walls of the chambers should be rigid. Most of the old chambers have a wooden supporting framework of vertical studding crowned with a wall plate rounded on the upper inside edge and beveled away outward below the round. The lead side curtains bend out over the round, are nailed down to the plate, and strapped to the vertical studding by lead straps. Seams are generally run vertically. Horizontal joints are made so that the upper sheet overlaps the lower on the inside, thus preventing leakage. The bottom sheets are laid across the chamber bottom and turn up inside and over a rim of side boarding 18 inches to 20 inches high. The side curtains usually are not attached to the bottom sheets, but the bottom edges of the side curtains are low enough to dip into the pool of acid maintained at the bottom. The ceiling lead is hung by lead straps to beams laid above. The ends of each ceiling extend out over the side sheet and are burned into the side sheets. Plate VII, *B*, shows an interior view of a lead chamber.

Most constructors now prefer steel framing with the chamber tops suspended from the roof of the building.

As variations in temperature expand and contract the lead walls, these should have curved corners and movable attachments to the framework to permit movement without buckling or bending of the sheets, particularly at the joint.

For bottom sheets, 8-pound lead is most commonly used, the edges being burned together. For side walls, 6-pound lead is used. The seams are burned with the sheets lying flat, and the whole section is then raised into position and the laps between successive sections are burned together. The top is usually of 6-pound lead. The method of hanging the top sheets in a plant of recent construction is shown in figure 7 and Plate VII, *C*. Lead straps are burned upon the 6-pound top sheets, and are turned to form an eye to receive a $\frac{1}{2}$ -inch iron bar, on the end of a threaded hanger with a special nut or washer resting on a pair of adjacent angle bars.

An average design of chamber affords a radiation surface of 10 to 15 square feet per 100 cubic feet of capacity, but, of course, the smaller the cross sections are in proportion to the length, the greater the radiation from a chamber. English practice provides about 20 square feet of radiating area per 100 cubic feet of volume capacity.

Flues for connecting chambers one with another, or for connecting chambers to an intermediate tower, may be circular or rectangular in cross section, according to the convenience in engineering. Experience has indicated that the height of the point of outlet or inlet of the gases is of no great consequence, as the natural circulation of the chambers is set up regardless of height of inlet and outlet.

The points in the chamber lining most severely attacked are usually around the entrances, where the reactions are more active than in other parts. Points not cooled by the outside air, such as the inner sheet of a lap joint, or points in contact with the timber framework are also subject to severe deterioration. Laying the chamber bottom on a slotted floor permits radiation of heat from the bottom sheets and serves to protect them. Most plants, however, carry considerable acid in the bottom, which, of course, protects the bottom sheets.

Acid storage tanks are usually provided beneath the chambers.

There are two special types of chamber plants in this country which should be mentioned briefly—the Falding high chamber and the Meyer tangential chamber.

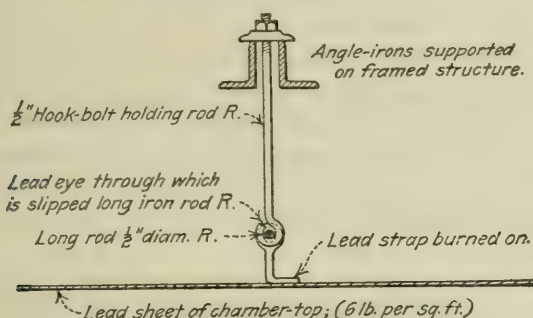


FIGURE 7.—Method of hanging top of lead chamber at a plant in Arizona. (By courtesy of Mining and Scientific Press.)

FALDING HIGH CHAMBERS.

The Falding high chambers, designed by F. J. Falding, were built to utilize as far as possible the mixing of the gases by the convection currents set up by the heat of the chamber reactions, and at the same time to maintain a zone of great chemical activity in the upper part of the chamber. If the chamber is high, the hot reacting gases will tend to rise and to remain at the top of the chamber so long as the reactions go on. The inert, nonreacting, nonheat-producing and therefore cooler gases tend to fall to the bottom of the chamber. The object aimed at was so to proportion the height and area of the chamber to the volume of gas admitted that there would be ample time and provision for the quantitative carrying out of the reactions, with the result that the gas drawn from the bottom would consist entirely of nitrogen oxides, inert nitrogen, and some oxygen. As the gases would leave the chamber too moist and too hot to permit their direct admission to the Gay-Lussac towers, they must be dried and cooled by a water-cooled tower situated between the chamber and the Gay-Lussac towers. The first

plant of this type was built at Vandergrift, Pa.; the plant comprised one chamber 50 feet square by 70 feet high, one Glover tower, two Gay-Lussac towers, and a small unpacked cooling tower 9.5 feet square by 50 feet high between the chamber and the Gay-Lussac towers.

At the plant of the Cleveland Cliffs Iron Co., at Marquette, Mich., there is one chamber 50 feet square by 70 feet high. The cooling towers, of which there are two, between the chamber and the Gay-Lussac tower, are 10 feet in diameter by 50 feet high. The capacity of this chamber plant is about 40 tons a day (50° B. basis).

The original acid plant at the smelter of the Tennessee Copper Co., at Copperhill, Tenn., comprises the largest installation of Falding chambers ever built. At that plant there are 11 chambers 50 by 50, by 67 feet high; 6 chambers 50 by 50, by 72 feet high; 4 chambers 22 by 50, by 77 feet high; 4 chambers 10 by 50, by 67 feet high; and 5 chambers 67 feet high but of varying lengths and breadths. The total chamber space in this set of chambers is 3,944,000 cubic feet.

As the chambers at the Tennessee Copper Co.'s plant are operating on blast-furnace gases, which vary greatly in composition, it is not possible to compare the results obtained with those obtained at other plants.

The greatest advantage of the Falding chamber is, of course, the great saving in lead. It is estimated that in the erection of a plant to contain 175,000 cubic feet chamber space, the Falding chamber will require 141,000 pounds of lead, and the usual rectangular horizontal chamber will require 240,000 to 300,000 pounds. There is also a considerable saving in ground space, which at some plants is a decided advantage. However, the cost of constructing the high chambers is greater than for the horizontal chambers, and the net saving in the total cost in most instances would be negligible.

No provision is made for obtaining an intimate mixture in the Falding chamber, other than the preliminary mixing brought about in the Glover tower and by the convection currents in the chamber, and no adequate means is provided for the condensation of the acid mist. Nevertheless, the results at the plants mentioned have been satisfactory; that is, there has been as complete a conversion of the sulphur dioxide, and the chamber space required has been as low, as at most horizontal plants; also the niter consumption has been reasonably low.

MEYER TANGENTIAL SYSTEM.

The Meyer tangential chamber is designed both to mix and to cool the reacting gases at the same time. The chamber is cylindrical in form, having approximately the same diameter as height. The gases

enter the chamber at a tangent near the upper part and leave the chamber through outlet pipes built in the center of the floor. The first chambers have water-cooled lead pipes suspended around the circumference, which aid to reduce the temperature of the gases. The spiral motion of the gases tends to mix them thoroughly, and this mixing, with the cooling of the gases by the lead pipes, serves to accelerate the reactions somewhat above the average rate in the ordinary horizontal chambers. Many ordinary horizontal chambers give as good results, however.

At the plant of the Griffith & Boyd Co., in Baltimore, Md., the Meyer chambers were 33 feet in diameter and 35 feet high.

At the plant of the Mountain Copper Co., at Martinez, Calif., the chambers were 39.4 feet in diameter and 42.6 feet high. A recent plant built at Fairmont, W. Va., has a chamber 46 feet in diameter and 70 feet high over all. The gases are delivered tangentially by three flues, 19½, 27, and 34½ inches in diameter, respectively, at a height of about 40 feet. The gases issue from the bottom of the chamber in three discharge flues, symmetrically situated, each flue being 20 inches in diameter. These flues discharge into a cooling tower 9 feet in diameter and 70 feet high, which acts as a cooling flue and spray catcher.

SPECIAL TYPES OF INTERMEDIATE OR REACTION TOWERS.

The conversion of sulphur dioxide into sulphuric acid takes place very quickly in the front part of the first chamber, nearly 70 per cent of the total reaction taking place within the first chamber and in the Glover tower. Then the reaction becomes slow and is again revived when the gases pass on into the next chamber. The increase in the rate of reaction as the gases pass from one chamber to the other is due partly to the increased mixing and partly to the gases and the mist particles coming into contact with cooled surfaces of lead. In this way the particles of nitrososulphuric acid mist, or particles of acid containing the nitrososulphuric acid, come into direct contact with the particles of cooled and condensed water mist, forming sulphuric acid and releasing nitrogen trioxide. Mere mixing of the gases alone will aid in the reaction, but by bringing the gases into contact with cooled surfaces, this reaction is even more efficiently brought about and the nitrogen trioxide more rapidly released for carrying on the process. The older authorities give many descriptions of various mixing appliances, ranging from Ward chambers partly filled with sheets of glass to Lunge plates, which are packed into columns inserted between the chambers.

Among the most practicable equipment used in the acid plants of this country for increasing the rate of mixing of the gases and for precipitating or condensing the mists of nitrosulphuric acid and

water as fast as they are formed are the following: Lunge plate tower; Gilchrist pipe columns system; Pratt converter system; Hoffman intensifiers; intermediate towers between chambers, as built by Chemical Construction Co.; and Anaconda "packed cell" system.

LUNGE PLATE TOWER.

The Lunge plate tower was one of the earliest developments of the intermediate "reaction" towers, designed to effect a constantly renewed mixture of all the gases, vapors, and misty particles, and to present large surfaces against which the gaseous current must strike in its course from one chamber to another. Described briefly, the plate tower comprises a lead tower, which may be either cylindrical or rectangular, filled with a series of perforated plates laid horizontally and spaced at some distance above the other. Each layer of plates is supported independently of the others. The plates are so constructed and placed that the holes in those of one layer do not come directly above the holes in the next layer below. As the hot chamber gases pass upward through the perforations in the plates they come into contact with dilute sulphuric acid splashing downward and also passing through the holes in the plates. The film of dilute acid over the plates presents an immense cooling surface to the gases and at the same time furnishes the water necessary for the decomposition of the nitrososulphuric acid.

The great disadvantage of this tower is its comparatively small cooling area and the high resistance that it interposes to the passage of the gases. A fuller description of the plate tower may be had by referring to Lunge's book.^a None of the modern plants in this country are equipped with plate towers.

GILCHRIST COLUMNS.

The Gilchrist pipe-column system for accelerating the chamber-process reaction was devised and patented by Peter S. Gilchrist, now president of the Chemical Construction Co., Charlotte, N. C. The columns are approximately 4 feet by 3 feet 6 inches by 15 feet high; are made of 9-pound or 10-pound lead, are supported in a wooden or steel frame placed about $2\frac{1}{2}$ feet above the floor level; and are built between the chambers, two or three to each chamber. The cubical content of the columns amounts to approximately 0.8 per cent of the total chamber space. The columns are filled with horizontal oval or angle pipes, with the outside deeply corrugated, so as to form recesses for acid on the top of the pipes. These deep corrugations increase the surface of the pipe for the gases to impinge upon,

^a Lunge, George, Sulphuric acid and alkali, vol. 1, pt. 2, ed. of 1913, pp. 656-673.

and offer greater obstruction to the gases as they wind their way upward through the columns. The pipes are staggered so that the course of the gases is continually interrupted as they reach each layer of pipes. The recesses or saucers formed by the corrugations on the top of the pipes fill with moisture or weak acid which overflows down the sides, cascading from pipe to pipe. On account of the continual and rapid mixing of the gases, the contact with the surface of the pipes, and with the weak acid flowing down over the pipes, the reactions take place quickly. There is always an excess of nitrous gases present, still further intensifying the rapid formation of the sulphuric acid. At the same time the gases are thoroughly mixed before entering the following chamber.

The intensive chemical reactions generate considerable heat which is carried off by cold air being drawn through the horizontal pipes by a natural stack draft. The acid produced runs down and through the converter into the chamber pan.

Pipe columns are installed at the plants of the F. S. Royster Guano Co. in Norfolk, Va., Columbia, Ga., Macon, Ga., and Baltimore, Md.; Morris Fertilizer Co., Atlanta, Ga.; Lowell Fertilizer Works, Lowell, Mass.; Mutual Chemical Co., Jersey City, N. J.; Standard Acid Works, Baltimore, Md.; Baugh Chemical Co., Baltimore, Md.; Maybank Fertilizer Co., Charleston, S. C.; Georgia Fertilizer Co., Columbus, Ga.; Robertson Fertilizer Co., Norfolk, Va.; Roanoke Guano Co., Roanoke, Ala.; Standard Acid & Fertilizer Co., Troy, Ala.; and others.

With this system the average plant can work very easily on 10 cubic feet of chamber plus tower space per pound of sulphur burned per 24 hours when burning pyrite, and can operate on 9 cubic feet when burning brimstone. Occasionally an even higher chamber-space efficiency is obtained.

PRATT CONVERTER SYSTEM.

The Pratt converter system was devised by N. P. Pratt, chemical engineer, of Atlanta, Ga., and patented in 1900 (U. S. patents 546596 and 652687). The patents have expired, but the Pratt Engineering Co., of Atlanta, Ga., has continued to make a specialty of building plants along lines similar to those of the original patents. An excellent description of the original investigations leading up to the establishment of the system is given in the *American Fertilizer*.^a

For the operation of the Pratt system at a plant having a capacity of about 60 tons of 50° B. acid per day, the general plan would be about as follows: A total chamber space of about 240,000 cubic feet would

^a Pratt, N. P., The N. P. Pratt converter system for the manufacture of sulphuric acid: *American Fertilizer*, vol. 13, July, 1900, pp. 33-42.

be provided, in three or four chambers, of which the first carries 80 per cent or 190,000 cubic feet. The other chambers have equal capacity, the main duty of these being to cool the residual gases on their way to the Gay-Lussac towers, and at the same time to trap and precipitate any acid mist that might pass to them. A lead-walled shaft or "converter" about 25 feet high and about 25 square feet square is installed near the rear of the first chamber. This shaft is packed with broken quartz, about the size of a man's fist or smaller, to within 18 inches of the top, the quartz packing resting upon grated chemical brick which rise about 2 feet above the pan. Through a wide, flat entry flue, connecting with the rear of the first chamber, part of the gases from the chamber is taken into the column just above the pan, the gases being drawn through the quartz-packed column by a large regulus metal or lead exhauster. The exhauster discharge may enter either the first chamber at the head or the flue leading from the Glover tower. If a fan is used to draw the furnace gases through the Glover tower and to discharge them into the first chamber and has sufficient capacity, the lead flue from the top of the quartz-packed column or "converter" can be connected directly into the flue from the Glover tower; then by suitable dampers in the Glover tower flue and the flue from the "converter" the relative volume of the gases from the two flues can be varied, giving a perfect control over the process. A flue from the front corner of the first chamber connects with the front of the second chamber, and the volume of gases passing from the first into the second is controlled by natural draft or by a fan at the end of the chamber system with capacity to carry through the chamber system the normal volume of gas. Thus, while the plant is in current operation, and is regulated in the usual way, the gaseous and misty contents of the large first chamber are moved rapidly through the length of the chamber and then pass up through the quartz packing of the converter, this movement being independent of and without any interference with the ordinary draft. The circulating capacity of the exhauster is much greater than the ordinary volume of gases coming from the Glover tower.

The water required for the process, except that supplied by the Glover towers, is usually supplied by feeding it under the brick grating of the quartz-packed column and at no other point.

If the volume of gases passed through the "converter" and circulating pipes is about 9,000 cubic feet per minute it is evident that with a main working chamber volume of 160,000 cubic feet a volume of gases equal to the entire content of the main chamber passes through the "converter" every 18 minutes. As a result of this intimate mixing in the chamber and the contact of the acid mist and water mist against the quartz packing of the column all the chamber

process reactions are accelerated and the activity of the nitrous acid (N_2O_3) is increased.

Plants equipped with this system have been operated with as low a chamber space as 7 cubic feet per pound of sulphur, to which, of course, must be added the volume of the flues, etc., in the system, making a total requirement of a little more than 7.5 cubic feet. The average plant on this system requires between 8.5 and 9.5 cubic feet of chamber space when treating a steady supply of gas of fairly high concentration, as from brimstone. Such results have been obtained with a yield of 4.8 pounds of 50° B. acid per pound of sulphur per 24 hours and with a niter consumption of 3.5 per cent, based on the weight of sulphur burned. The use of the Pratt system, of course, requires excess power above what is required at any ordinary chamber plant.

Most of the plants operating with the Pratt converter system are in the South, but in the last few years a number of such systems have been installed in the North, chief among these northern plants being the Armour Fertilizer Works, Chrome, N. J., and the Butterworth Judson Corporation, Newark, N. J.

INTERMEDIATE TOWERS BUILT BY CHEMICAL CONSTRUCTION CO.

The intermediate towers designed by the Chemical Construction Co. are lead-lined towers, with steel frames and packed with 6-inch "chemico" spiral rings, as described on page 87. The 6-inch rings have a surface area of 27 square feet per cubic foot of packing, with 60 per cent free space for passage of the gases. The rings are placed in the tower in layers, each layer being staggered. The gases pass up through the rings largely in a spiral motion, thereby remaining in the tower longer than with a direct line of travel, and at the same time causing the up-going gases and the down-coming acids to remain in contact with each other for a long time and over a large surface.

With this type of packing there is claimed (1) intensive mixing of the gases, owing to the whirling motion imparted, (2) large contact surface, (3) large free space, and (4) durability. The whirling motion evidently is not perfect, as there is a space about three-fourths of an inch in diameter through the center of each ring, through which gases and liquids may travel vertically without going around the spiral, also spaces between the adjacent rings permit the vertical flow of acids and gases.

The acid formed in the tower runs down the surface of the spirals and sides of the rings, keeping the surfaces always moist. Water sprays are used in the inlet pipes to keep the strength of the acid down to a normal working basis, as otherwise the strong acid would

absorb the nitrous oxides present. On account of the large area of surface exposed and the intimate mixing of the gases by the spiral motion, the reaction in the tower is vigorous and a relatively large amount of acid is produced.

These intermediate towers have been installed at the plant of the Alabama Chemical Co. at Montgomery, Ala., and of Swift & Co. at Harvey, La.

The following data has been furnished by the Chemical Construction Co. relative to the work of the intermediate towers at the Swift & Co. plant:

Data on intermediate towers at Swift & Co. plant.

	Cubic feet.
Total chamber space in five chambers.....	268,500
Intermediate towers between each chamber (28 feet high by 6 feet wide by 24 feet 9 inches long), each.....	4,158
Volume space in four intermediate towers.....	16,632
Tower at rear of last chamber (14 feet high by 5 feet wide by 15 feet 3 inches long).....	1,068
Total cubic feet in towers.....	17,700

Ratio of tower volume to chamber volume = $\frac{17,700}{268,500} = 6.5$ per cent.

Ratio of open space in towers to chamber space = $\frac{17,700 \times 0.60}{268,500} = 3.9$ per cent.

First tower—that is, the one between the first and second chambers—produces 16,905 pounds of 55°B. acid at 197° F., or 21,064 pounds 50°B. acid, equivalent to 4,434 pounds of sulphur.

Efficiency of first tower, therefore, is $\frac{4.158}{4,434} = 0.938$ cubic feet of tower capacity per pound of sulphur burned daily.

Total amount of 50°B. acid produced in five towers is 60,700 pounds, equivalent to 12,900 pounds of sulphur. Tower capacity required per pound of sulphur converted per 24 hours in total tower installation, is 1.37 cubic feet.

Total production of entire plant is 180,000 pounds of 50°B. acid per day.

Amount made in towers, 60,000 pounds, equivalent to 33½ per cent.

Amount made in chambers, 120,000 pounds.

Efficiency of chambers alone is 10.7 cubic feet per pound of sulphur burned per 24 hours.

Total efficiency of whole plant—that is, chamber plus tower capacity—is 7.6 cubic feet per pound of sulphur.

The Chemical Construction Co. are now designing towers of much larger capacity than those described, and at the same time reducing the chamber capacity proportionately. The towers are designed to have a height of about that of the chambers, a width of 5 to 10 feet, and length according to the work required. The special rings are made of chemical and acid proof brick and are claimed to be practically indestructible.

Figures 8 and 9 show the types of plant with the intermediate towers recommended by the Chemical Construction Co. It is to be noted that the arrangement is similar to that recommended by practically all construction companies and common to all modern plants—that is, the roaster, dust chambers, niter ovens, the Glover tower, and the Gay-Lussac towers, are all concentrated at one end of the plant. Thus, in a six-chamber plant the gases after passing ahead through three lead chambers, double back through the other three chambers parallel to the first three, to the Gay-Lussac towers. This arrangement facilitates technical control as well as convenience in operation.

It is evident that the main consideration to be given any scheme for intensifying or increasing the rapidity of the reactions in the chamber process is whether or not the increased cost of installing and operation as compared with the cost for an ordinary chamber plant is justified by the results obtained. In other words, it is not so important to obtain a high conversion factor per unit volume of chamber, or tower space, as it is to obtain the largest conversion per unit cost of investment or of operation. At certain skillfully operated plants, equipped with ordinary chambers without any intermediate towers other than cooling towers, results obtained have been nearly if not just as satisfactory as those obtained at other plants equipped with intensifiers or intermediate towers, but less skillfully controlled.

ANACONDA "PACKED-CELL" PLANT.

At the acid plant of the Anaconda Copper Mining Co., at Anaconda, Mont., there has been developed during the last year a successful process for the manufacture of acid, called the "packed-cell" process. The main features of the process were devised by E. L. Larison, superintendent of the acid plant at Anaconda, who has applied for a patent. After experiments had been conducted on a laboratory scale, the process was tried out on a 2-ton scale. On the satisfactory performance of this 2-ton experimental plant the Anaconda company authorized the erection of a 25-ton plant, which has recently been completed and is now in successful operation.

In this new plant the lead chambers are entirely eliminated and in their place are substituted brick cells, or towers, packed with acid-proof brick or other packing to create vigorous mixing of the gases and mists, and to afford large surfaces upon which the gases may impinge. This packing is kept wet with cold sulphuric acid of such gravity that it will not take into solution the oxides of nitrogen. The acid carries off the heat of the reaction, and in fact, controls it. One of the causes for the nonsuccess of earlier forms of reaction

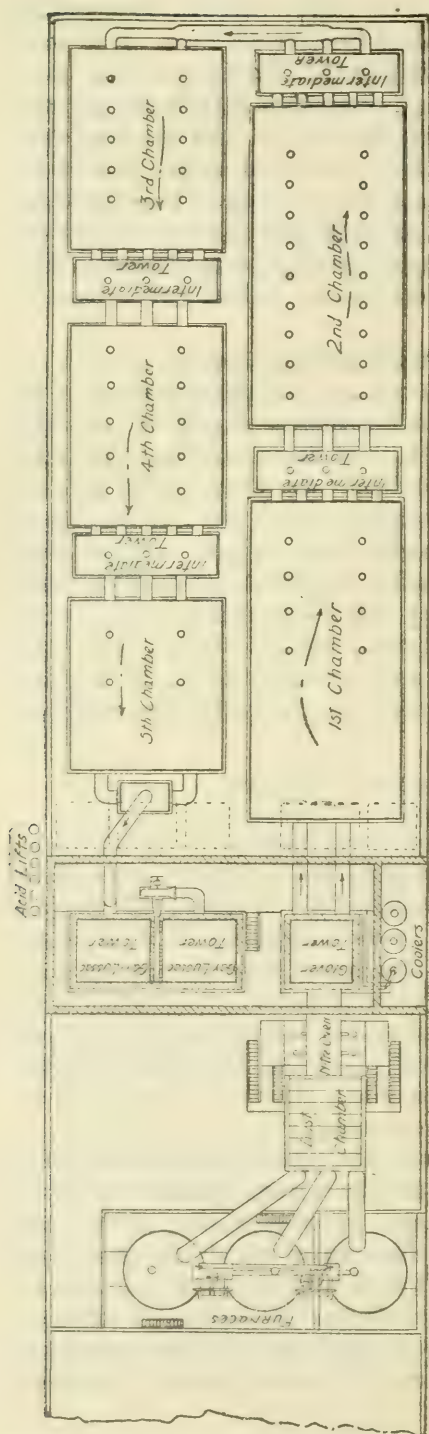


FIGURE 8.—Plan of chamber plant designed by Chemical Construction Co.

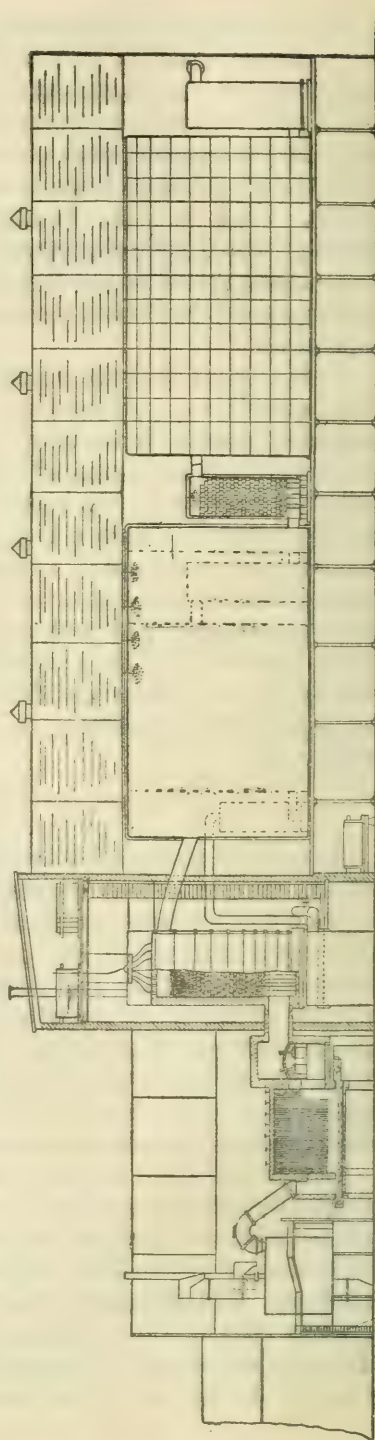


FIGURE 9.—Elevation of chamber plant designed by Chemical Construction Co.

towers was due to the inability to get rid of the heat generated in the towers. This feature has been solved at Anaconda by the large volume of acid being circulated, amounting to ten times the total acid made in the tower. The acid issues hot, is cooled, pumped up, and reintroduced. The tower capacity required is only about 1 cubic foot per pound of sulphur per 24 hours.

DESCRIPTION OF PLANT.

A brief detailed description of the plant, as given by the Anaconda Copper Mining Co., follows:

Flues and blowers.—The gas is drawn from the furnace dust chamber through a 24-inch asbestos-covered steel flue. The blower is a No. 11 Buffalo forge blower, provided with a water-cooled gland, where the shaft enters the case, and with water-cooled bearings. This blower runs at about 750 r. p. m. and is very satisfactory.

Glover tower.—The Glover tower is of standard dimensions and design. It is sheathed with lead. Splash-plate acid distributors are used. Two 4-foot by 4-foot by 4-foot coolers take the outflow. Each has four 1½-inch pipe coils.

Reaction towers or cells.—There are five reaction cells built in a block. They are sheathed with lead. They are packed with Anaconda slime brick of standard shape and size. Acid is made in them at the rate of about 1 pound of sulphur converted per cubic foot of packed volume. Each cell is provided with its individual acid-distributor system. The acid issues from each cell into a launder and is conducted to a set of coolers, then elevated by a centrifugal pump to the distributing box as needed. The gravity of the acid leaving the cells is maintained at such a point that it will neither absorb the nitrogen oxides nor the sulphur dioxide. The distributing and cooling arrangement permits good regulation of the gas temperature in each cell.

Gay-Lussac towers.—The Gay-Lussac towers, two in number, are built in one block with an interior downtake flue between them. The block is lead sheathed. The volume and general design is conventional. Splash-plate distributors are used.

The acid throughout the whole plant is pumped by Lewis vertical submerged centrifugal pumps with direct-connected motors. The pumps for the circulation of tower acid (that is, 60° to 61° B. acid) are of iron. The weak-acid pumps are lead covered. Iron tanks and pipes are used for the 60°–61° B. acid and lead for the weak acid. Four pumps are used, each equipped with a 5-h. p. motor; they have a large margin of excess capacity.

It should be mentioned that part of the rapidity of reaction is due to the use of more than twice the usual niter circulation, being nearly 70 parts of sodium nitrate per 100 parts of sulphur. This is possible on account of the temperature control that is effected in the reaction cells by means of the circulation of acid.

An unusual construction feature is in the manner of applying the lead and supporting it. Instead of building a strong steel frame and hanging the lead, and then putting in the masonry walls and packing, as is ordinarily done, the masonry was all erected first and then the lead applied. The lead sheets are attached to compara-

tively light framing, and this in turn is supported where necessary on corbeled shelves extending from the faces of the transverse walls. All heavy steel and wood columns are done away with and the lead is carried by the masonry, which is amply strong to support it.

The brick used for walls and packing is Anaconda slime brick, being made from the slime tailings from the concentrating mill. The mortar is made of 30° B. silicate of soda with 100-mesh "Dillon rock," a pure natural quartz quarried near by. The walls were laid carefully, but not especially so. The average rate of laying per day per mason was 800 brick. It was originally considered that such a plant might be built without lead sheathing, but it developed that absolutely tight walls could be built only by using the most perfectly uniform brick and by laying them with a degree of care and consequent slowness that made the cost far higher than sheathing with lead. Future plants may be built entirely with lead walls supported by steel framework, doing away with the interior brick walls.

Needless to say, no housing is necessary to protect the lead from wind and weather. A top house to protect the operator and a shed to protect the tanks and pumps are the only buildings necessary.

Figures 10 and 11 show the plan and elevation, respectively, of the 25-ton plant. Plate VIII shows the form of packing. Plate IX shows the 25-ton plant under construction before the brick walls were covered with the lead sheathing.

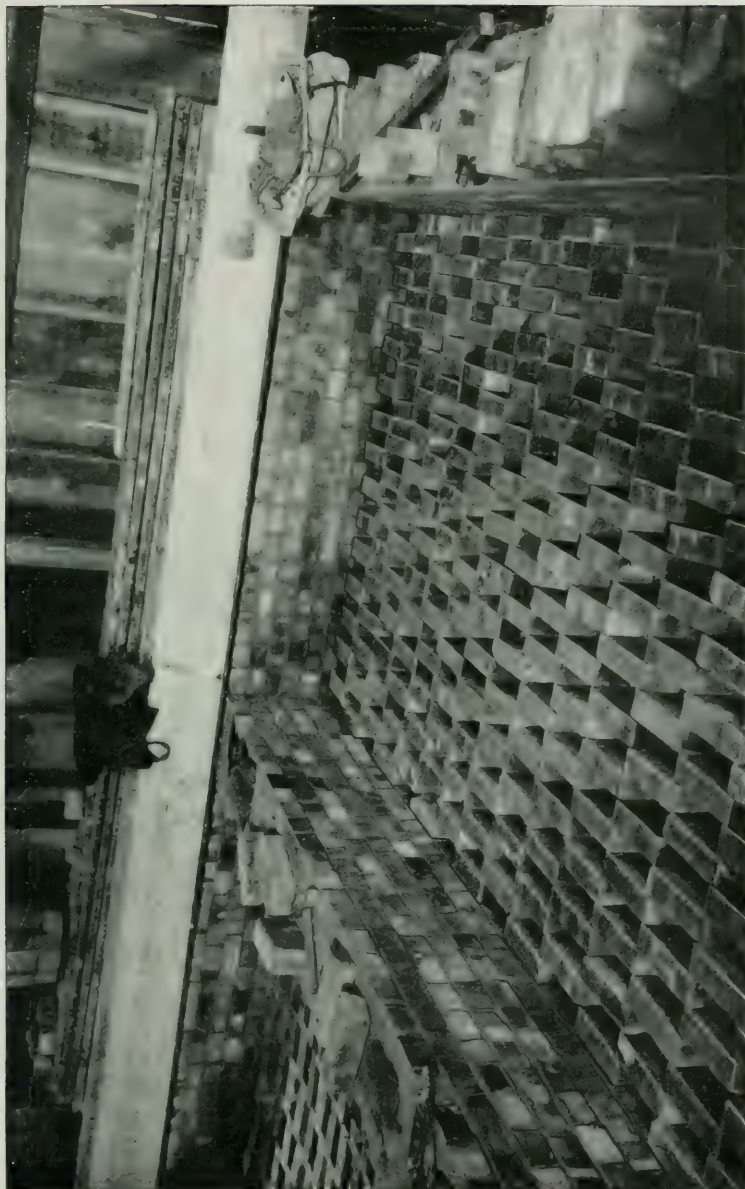
The 25-ton plant occupies a ground space of about 40 by 80 feet, including tanks, pumps, and other equipment.

OPERATION.

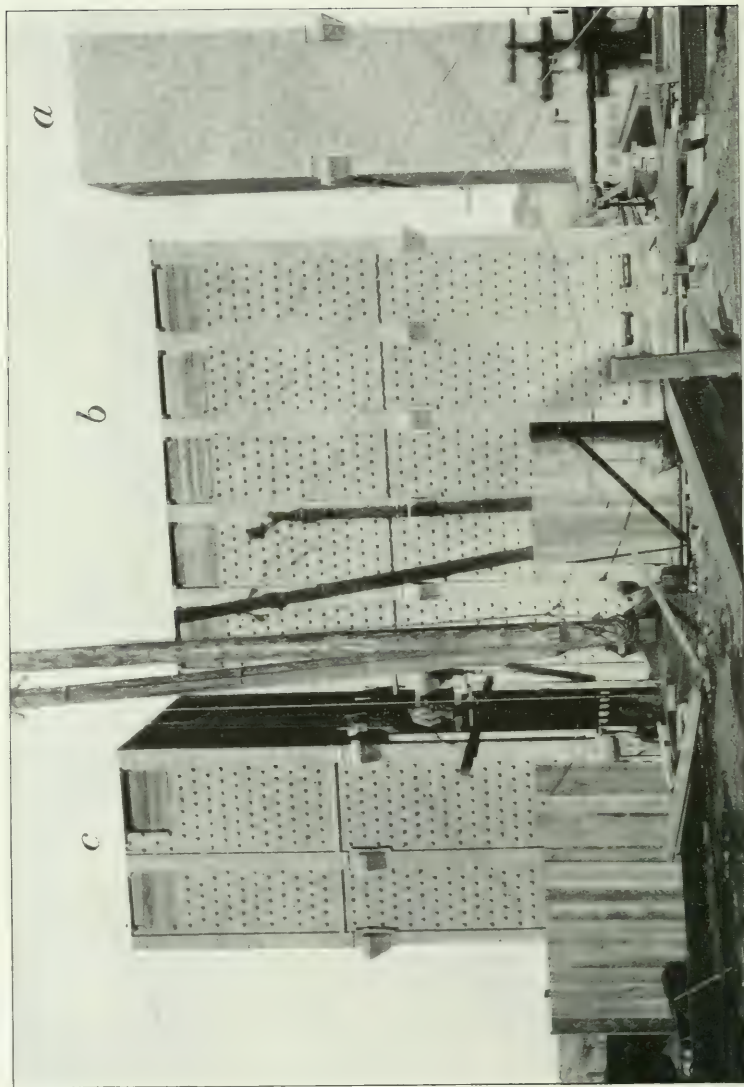
Operation is controlled by sulphur dioxide tests of the gases entering the first and fourth cells, and nitrous vitriol, temperature, and hydrometer tests at various points.

Control work is done by one man. A second man oils, cleans up, and acts as general factor of safety. It seems from the compactness and simplicity of operation of this plant that a 100 or 150 ton plant could be as readily handled by two men.

The niter consumption at the start of the operation of this plant has been considerably higher than with the ordinary plant, being about 6 per cent as against 4.5 per cent in the chamber plant close by. A large proportion of the consumption is due to mechanical losses, caused by fluctuations in the gas concentration. The niter loss is being gradually decreased as the best conditions as to cell temperatures and acid strengths are being determined. However, the reconversion of the lower nitrous oxides into the higher oxides, which are readily recovered by the Gay-Lussac tower acid, seems to require



VIEW OF TOWER OF ANACONDA ACID PLANT DURING CONSTRUCTION, SHOWING PACKING.



VIEW OF ANACONDA ACID PLANT DURING CONSTRUCTION, BEFORE TOWERS WERE COVERED WITH LEAD.
a, Glover tower; *b*, five packed reaction towers; *c*, Gay-Lussac towers.

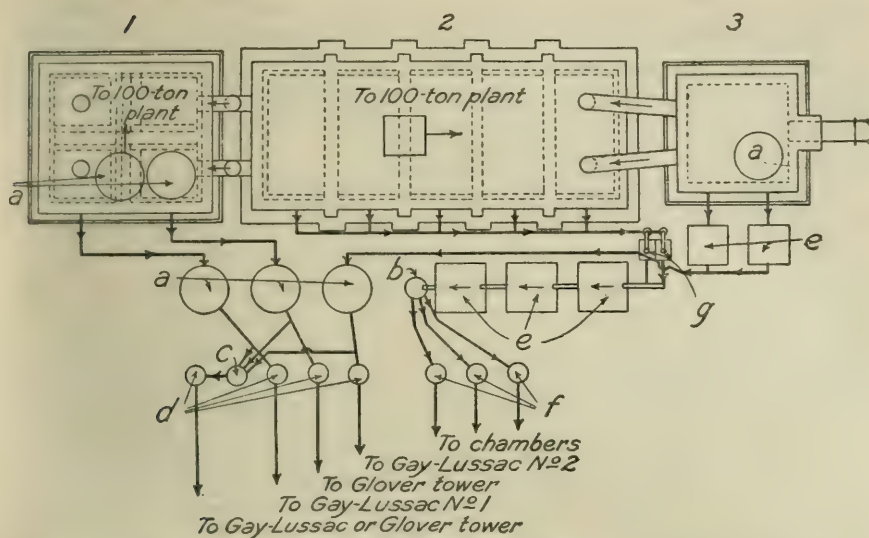


FIGURE 10.—Plan of Anaconda acid plant with packed tower: 1, Gay-Lussac tower (2 compartments); 2, chamber compartments; 3, Glover tower; a, iron tanks; b, distributor; c, collector; d, iron pump; e, coolers; f, lead pumps; g, air lifts.

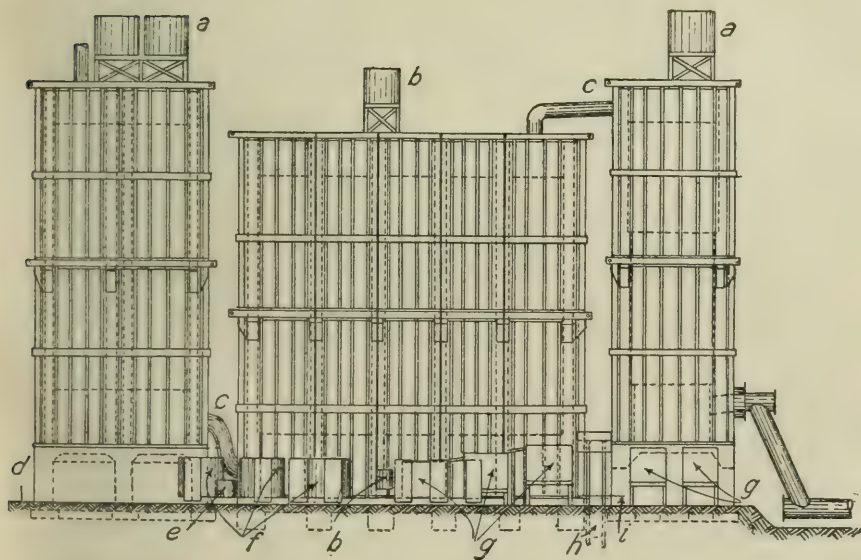


FIGURE 11.—Elevation of Anaconda acid plant with packed tower: a, circulating tank; b, distributor; c, lead flues; d, top of foundation for Gay-Lussac tower; e, collector; f, iron tanks; g, cooler; h, air lifts; i, top of chamber foundations.

some time, and the introduction of a chamber, probably of comparatively small capacity, between the reaction towers and the Gay-Lussac towers may be necessary in order to give the time required for a satisfactory niter recovery. Recent work has shown that the use of a third Gay-Lussac tower would increase the niter recovery to a point where the resulting loss would be normal.

The main advantage of this type of plant over the ordinary chamber plant is the decreased cost of construction. At Anaconda, where acid-proof brick can be made at a fairly low cost—about \$8 per 1,000 with 1916 prices—and lead construction is relatively high, the cost of this type of plant is about 45 per cent of that of a chamber plant. At other points where the cost of brick is greater and the cost of lead construction less, the difference would not be as great, but the cost would in all cases be less than for a lead chamber of corresponding capacity. The cost of operation per ton of acid produced apparently will be about the same. The cost of maintenance of the packed cells remains to be demonstrated, but indications are that it will be less than that of maintaining a lead chamber plant.

GAY-LUSSAC TOWERS.

In order to recover the oxides of nitrogen issuing from the last chamber, the gases are led into Gay-Lussac towers where these oxides are absorbed by moderately concentrated (60° to 62° B.) sulphuric acid. Nitrous acid (N_2O_3) is absorbed with the formation of nitrososulphuric acid. Nitric oxide (NO) is not absorbed except in the presence of oxygen when the higher nitrogen oxides are formed, hence the necessity of maintaining a certain proportion (about 5, per cent) of oxygen in the exit gases. Nitrogen peroxide (N_2O_4) is absorbed slowly by the acid with the formation of nitrososulphuric acid and nitric acid. When nitric oxide and nitrogen peroxide are present in the proper proportions and sufficient time is allowed for the reaction, the result is a nearly complete conversion to nitrous acid, which is readily soluble in sulphuric acid.

Some acid experts maintain that the presence of a certain proportion of sulphur dioxide is necessary in the exist gases from the last chamber in order to keep a sufficient proportion of the higher oxides of nitrogen reduced to nitric oxide to permit conversion of all the nitrogen peroxide to nitrous acid. In "forcing" the chamber and operating with a high niter circulation there may undoubtedly be considerable nitrogen peroxide in the gases, and unless the capacity of the Gay-Lussac towers is adequate to allow the longer time for absorption of the peroxide, it would undoubtedly be lost. This loss may be prevented by the presence of a small amount of sulphur dioxide to react with the nitrogen peroxide, as outlined above.

On the other hand, if too much sulphur dioxide is present in the gas mixture entering the Gay-Lussac towers, nitric oxide forms in excess of the quantity needed to form nitrous acid with the nitrogen peroxide, or in excess of what can readily be oxidized to nitrous acid. As nitric oxide is only slightly soluble in cold sulphuric acid of 60° B. strength, this excess will be largely lost, and as nitric oxide is a colorless gas, its loss will not be so readily detected by observing the gases escaping from the top of the tower.

CONSTRUCTION OF TOWERS.

Various styles of Gay-Lussac towers with different types of tower packing have been proposed. The most commonly used type is a lead tower much higher than it is wide, of circular or rectangular form, and filled with a tower packing, such as coke, quartz, or acid-proof stoneware. The packing is so arranged that the stream of sulphuric acid solution entering from above is broken into small drops or spray as it descends through the packing. The gases rise in numerous small streams, through the interstices of the packing, so that the surface of contact between acid and gas is as large as possible.

The capacity of the tower corresponds in a measure with the capacity of the chambers and also with the method of operation. Intensive working of the chambers, involving a high niter circulation, requires a larger tower capacity than a more moderate method of working. Thus, when the plant is so operated as to use 16 to 20 cubic feet of chamber space per pound of sulphur burned per 24 hours, a Gay-Lussac tower capacity equivalent to 2 per cent of the chamber space is usually sufficient. With more intensive working, the tower capacity must be increased, even to 3 or 3.5 per cent. These figures refer to the space occupied by the packing and the interstices, not to the total space in the lead shell. However, the efficiency of the Gay-Lussac tower is more largely dependent on the condition of the entering gas, as discussed previously, and upon the method of constructing and packing, than upon any absolute ratio of cubic content to chamber space. The distribution of the acid throughout the tower should be as perfect as possible.

With the large Gay-Lussac tower capacity required at many works, it is impossible to use only one tower. In many plants two towers are employed, the first being fed with the acid from the second. In both towers, the gases should ascend against the stream of acid.

Gay-Lussac towers, as previously stated, have recently been built of chemical brick laid in acid-proof cement (see fig. 12), in lieu of lead. In building towers of chemical brick the horizontal and vertical joints of the brick in the walls are staggered, and on the inside two layers of 6-inch by 6-inch tile are placed also with staggered joints. This

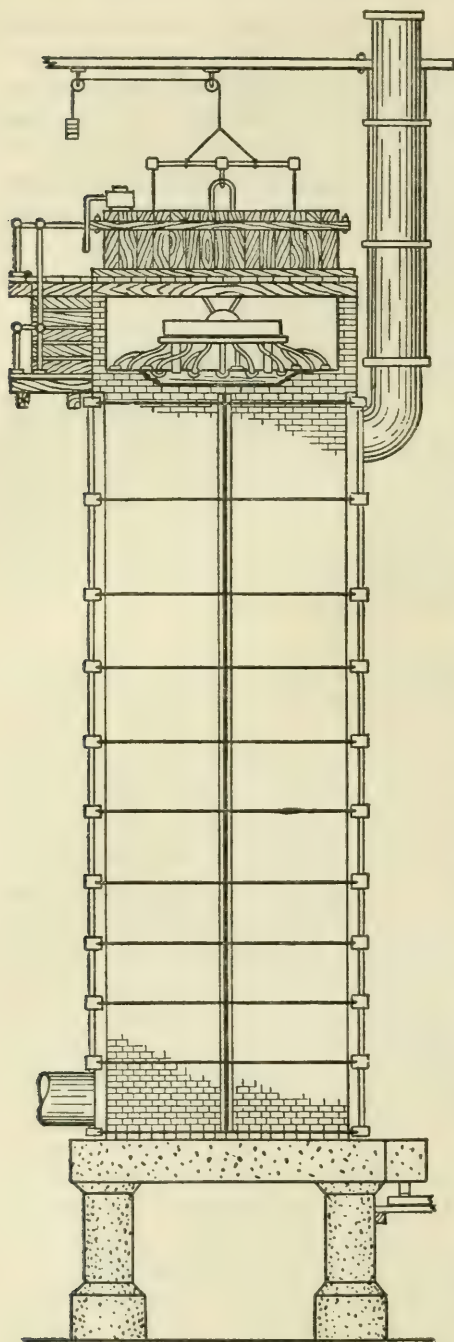
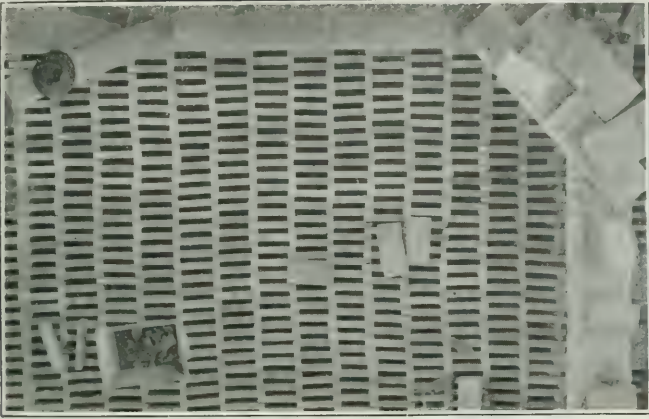


FIGURE 12.—Typical masonry, Gay-Lussac tower.

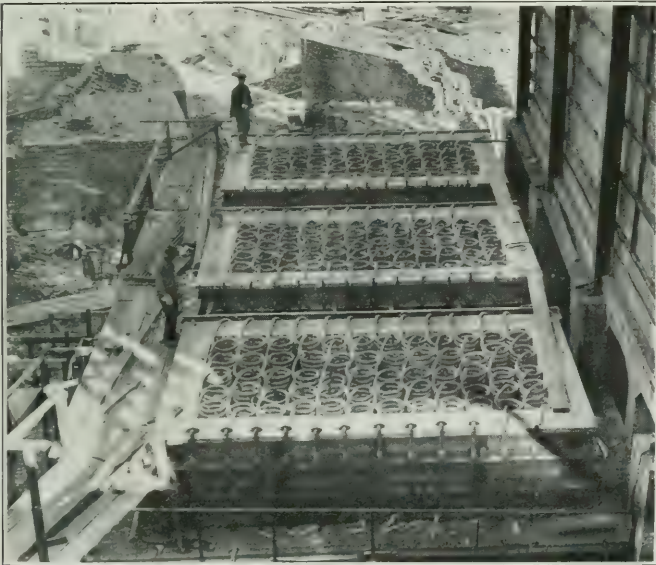
method practically eliminates acid or gas leakage. In this construction the connecting flues between the brick towers are also of chemical brick in place of lead.

At the acid plant of the Calumet and Arizona Mining Co., a radical departure from the usual type of construction has been introduced. There are 12 towers built into a solid block, each tower being 13 feet square by 45 feet high. The towers are built of duro brick laid in duro cement, and the interior is packed with duro tile. (See Pl. X, A.) The entire block of towers is inclosed in lead sheeting, hung upon a steel frame. The stream of gases coming from the chambers is divided into three parts, each part passing independently through a series of four towers. The cold acid from the Glover tower is pumped to the top of the fourth tower, and travels counter current to the gases.

At the plant of the Tennessee Copper Co. is a Gay-Lussac tower of peculiar construction. There is only one tower for a series of four chambers aggregating 557,000 cubic feet of chamber space. This tower is built of acid-proof brick laid in acid-proof cement, without lead curtains. The tower is divided into 56 cells, the partitions being of acid-proof brick. There are eight parallel rows of cells and seven cells to the row. Each cell is 8 feet square inside, with a total height of 40 feet.



A. DURO TILE PACKING OF GAY-LUSSAC TOWER.



B. COOLING TANKS AT PLANT OF CALUMET & ARIZONA MINING CO.

(By courtesy of the Mining and Scientific Press.)

The gases traverse the eight rows in parallel, passing up one cell and down the next until they arrive at the top of the seventh cell, when they are drawn through the back fan and discharged into the exit stack. The acid is distributed over the tops of the cells by means of a single acid feed pipe to each cell, terminating inside the tower in a sprayer provided with a splash plate that sprinkles the acid with approximate uniformity over the entire top of the tower packing. The lead pan at the bottom is divided into three compartments by means of brick partitions whereby it is possible to keep separate nitrous vitriol of three different grades of nitrosity, as discharged from the tower. The 56 cells are divided into three series, as to the circulation of acid—the first having 24 cells, the second and third having 16 cells each—and the acid in the three compartments progresses forward through these series.

No advantage from this type of construction has been experienced, and, in fact, owing to the difficulty in the working of the cells when they become clogged, they have been rather disadvantageous to operate.

One of the advantages in operating two or more towers in series is that if any irregularity occurs in the chamber operations whereby some sulphur dioxide is admitted into the first Gay-Lussac tower, the nitrous and nitric oxides escaping as a result from the first tower can be recovered in the second. A tower of considerable height would of course accomplish the same result but the expense of building such a tower would be too great.

PACKING.

It has been the general custom in the past to pack the towers with coke, using hard-burnt oven coke. Soft, porous coke is not satisfactory, as it can not support the pressure of the column and is acted upon by the nitrous vitriol too readily. In fact, even hard-burnt coke is slowly acted upon by nitrous vitriol, or by the nitrous or nitric acid, and so deteriorates in time that the towers must be repacked. Some coke towers require repacking every year. The efficiency of coke packing has been rather overestimated, for, as a matter of fact, the pores of the coke become filled with acid so that only the exterior of the lumps remain effective in presenting a film of acid to the gases. Tile, such as duro tile, and special chemical earthenware shapes, such as the "chemico" spiral rings, are now being largely used.

ACID SUPPLY.

The supply of cold acid to the Gay-Lussac tower should be as regular and as evenly distributed over the entire cross section as

possible. Various devices are employed for this purpose, which need not be described here. The most commonly used is the "splash plate" distributing device. The acid is usually pumped into storage tanks built at a high elevation, and thence to the distributors, or may be pumped directly to the distributors. The supply is so regulated that the nitrous vitriol, coming from the bottom of the Gay-Lussac tower nearest to the chamber, will have in solution an amount of N_2O_3 equivalent to 40 to 60 ounces of sodium nitrate per cubic foot of acid. The nitrous vitriol should not contain less than 1 per cent N_2O_3 , or the equivalent of 36 ounces $NaNO_3$ per cubic foot of acid. Above a strength of $2\frac{1}{2}$ per cent N_2O_3 , or the equivalent of 90 ounces per cubic foot of acid, there is some danger of a loss of niter from the acid.

From the Gay-Lussac tower the nitrous vitriol is pumped into storage tanks for feeding it to the Glover tower.

EXIT GASES.

The exist gases issuing from the Gay-Lussac towers, when ample tower capacity is provided, are never free from sulphur dioxide or nitrogen oxides. Usually the gas issuing from the tower has an orange color, which is probably due to the oxidation of some residual nitric oxide (NO) to nitrogen peroxide (N_2O_4) in contact with the air. With a single Gay-Lussac tower there is also some slight loss of nitrous acid (N_2O_3) due to the vapor tension of nitrous acid or of nitrososulphuric acid in sulphuric acid.

NITER SUPPLY.

From the formulas representing the chamber process reactions it would appear as though, once sufficient niter was added to the plant further quantities would not be required. However, for various reasons, there is a loss, and it is necessary to replenish the supply.

The quantity of niter lost in the working of a chamber plant varies greatly, depending largely upon (1) the adequacy of the Gay-Lussac tower capacity with regard to the chambers and to the intensity of working, (2) the regularity of the supply and concentration of the gases from the burners or other source of supply, and (3) the skill of the operators in maintaining regular and controlled reactions in the chambers. Even with the best practice there is always some loss, partly mechanical and partly chemical. The mechanical loss is caused by small amounts of some of the oxides being carried through the Gay-Lussac towers by the waste gases; also a small amount is lost by solution in the chamber and Glover tower acid. The chemical loss is due to the formation of oxides which are not dissolved in the acid.

In average practice in this country, when running on a good grade of pyrite or a brimstone, the niter loss is around 4 per cent of the sulphur burned. At a number of plants the consumption is less than 4 per cent, and claims have been made that certain plants have been operated for a period of months with less than 2 per cent niter consumption. A niter consumption of around 3 per cent may be taken as very good practice.

At plants utilizing waste gases from metallurgical operations, the niter consumption is frequently much higher and at one plant has been as high as 8 or 9 per cent for long periods, this being due to the widely fluctuating composition of the gases.

As has been already stated, the ideal method of introducing the necessary niter to make up for that lost is by "potting" the niter, allowing the distilled nitric acid to be absorbed by sulphuric acid maintained at a temperature to prevent loss of nitrogen oxides, and then adding this mixture to the Glover tower. Another method is to add the nitric acid directly to the Glover tower.

The common method of adding the niter is to "pot" it, the nitric acid being introduced directly as vapor into the gases as they pass along the flues leading to the Glover tower. Usually the nitric acid vapor is generated in cast-iron pots placed in an enlarged part of the main flue, called the "niter oven," suitable supports for the pots being provided. Nitrate of soda and sulphuric acid are charged into the niter pot and the reaction between the two is aided by the heat of the gases. Shallow cast-iron pans are usually provided below the pots to catch the material that boils or slops over. The nitric acid gas issuing from the pot is converted into nitrous acid gas by the sulphur dioxide in the gases. The liquid residue, "niter cake" (NaHSO_4 , or a mixture of Na_2SO_4 , H_2SO_4 and NaHSO_4), is tapped through pipes provided for the purpose into molds. The use of this niter cake is discussed in a subsequent connection (p. 207). The main disadvantage of this method of adding the niter is the fact that the niter is added in large "doses" at intervals. In a large plant, of course, where a number of pots are used, the charging and discharging of the pots can be so regulated as to produce a fairly constant and regular supply of the nitrous oxides.

In some plants, the standard retort as used in the manufacture of nitric acid is employed, these retorts being placed outside the flue and fired with coal.

At the plant of the Tennessee Copper Co. the retorts are 10 feet high and 8 feet in diameter, large enough to cook a charge of 8,000 pounds of nitrate of soda. The nitrate is fed automatically and at the same time the sulphuric acid is added in the requisite amounts by an automatic feeder acting in conjunction with the nitrate feeder.

In the manufacture of nitric acid for commercial purposes a certain proportion of the nitric acid produced is too weak or too impure to be marketable. There is also a considerable loss of non-condensed oxides of nitrogen both in the manufacture of nitric acid and of mixed acid, which can best be saved by passing the first exit gases through a scrubber or tower and absorbing the contained nitrous acid in sulphuric acid, forming nitrous vitriol. This weak or impure acid and the nitrous vitriol can be utilized for supplying the chambers with nitrous acid gases by means of the Glover towers.

Nitrous acid gas from various chemical works, and the spent acid from other industries, can be run into the Glover tower and utilized.

COOLING TANKS.

The sulphuric acid from the bottom of the Glover towers will be hot, usually about 120° to 130° C., and in some instances when the furnace gases are especially hot and the volume of gases is large for the Glover towers the temperature may be 150° C. This acid must be cooled before storage or before being used in the Gay-Lussac tower for the absorption of nitrous oxides. For this purpose, cooling tanks or worms are usually placed near the Glover towers on a level below the bottom of these towers, so that the acid will flow by gravity to the tanks or worms. The tanks are frequently of wood, lined with 6-pound lead, containing coils of 1-inch lead pipe, provided at the inlet end with a Buchner or silica funnel extending down into the end of the coil below the surface of the water. In this way the hot acid is not delivered to the lead pipe before the pipe is cooled on the other side by water, thus reducing the wear and tear on the lead coolers. The cooling tanks may be built in a group with lead partitions. The various turns of the lead coil are separated by flat iron spreaders which are suitably bolted together in order to make the coil a rigid unit.

In other types of coolers, where water is abundant, the lead-lined tanks are filled with the acid and the cooling water is circulated through lead coils. The coils are built in sections, each section being independently supplied with cold water. The lower coils are kept cooler than the upper and the cold acid collected at the bottom of the tank is drawn off by an insulated siphon to the storage tanks.

Various designs of coolers are in use, according to the conditions at the different plants, but the general principles are the same.

At the plant of the Tennessee Copper Co., where there are about 3,600 tons of acid per day to be cooled from 150° to 35° C., there are nine coolers, rectangular in shape, the inside dimensions being 17 feet long by 8 feet 6 inches wide by 4 feet 8 inches deep. The framework is of steel channels placed edgewise to the cooler, supporting a shell of 15-pound lead, which is lined with 9 inches of

acid-proof brick laid in acid-proof cement. Each cooler contains 71 coils of $1\frac{1}{2}$ -inch lead pipe, the coils being 12 inches in diameter. In the nine coolers there are more than 6 miles of $1\frac{1}{2}$ -inch lead pipe. The coolers are placed in two terraces so that the acid may flow from one series of cooler to the other.

At the modern plant of the Calumet & Arizona Mining Co., the cooling tanks are built with steel frames, and are lined with 6-pound lead sheeting, which is also lined with 4 inches of duro brick laid in duro cement. The tanks are 16 inches by 99 feet by 5 feet and each tank contains 5,000 feet of lead pipe, $1\frac{1}{2}$ inches in diameter with $\frac{1}{2}$ -inch walls. Instead of being built in large coils, the lead pipe is in small coils 15 inches in diameter. Each coil is independent of the other. These coils are placed in tanks with the central axis in a vertical position. (See Plate X, *B*, p. 116.)

In general, cooling of the acid is required only for the Glover tower. However, at plants where the Gay-Lussac tower acid is to be recirculated, or one portion of it is used in an intermediate tower, frequently this acid is also cooled.

ACID CIRCULATING SYSTEM.

The amount of acid that must be circulated around a chamber-plant system is very large. The amount of acid used over the Gay-Lussac tower will vary between 100 and 300 per cent of the acid produced in the chambers. This acid must be pumped to the top of each of the Gay-Lussac towers, where there are more than one, and also pumped to the top of the Glover tower. In addition, part or all of the chamber acid is pumped to the top of the Glover tower, and when intermediate-reaction towers are used, there is also more or less pumping in connection with these.

For pumping and circulating these quantities of acid, various devices have been employed, chief among them being the compressed-air lift in connection with an acid "egg" or "blow case." The "eggs" are usually cast-iron cylinders of different sizes having rounded ends and supplied with three pipe openings. The "egg" is filled with acid through one pipe containing a check valve, which prevents return of the acid when the pressure is applied. Compressed air is admitted through another pipe. A third pipe, extending to the bottom of the egg, permits the acid to leave the vessel under pressure, followed by a volume of air equal to or slightly greater than the compressed volume.

The Kestner automatic elevator (fig. 13) manufactured by the Bethlehem Foundry & Machine Co. has been used for years at many of the largest acid plants with satisfactory results. Acid runs from tank *a* through the valve *e* to the pulsometer *b*. When this is filled, the

acid lifts up the float *f*, whereby the rod *c* opens the inlet valve in the air distributor *d* and shuts the outlet valve, so that the air forces the acid upward in pipe *h*. Part of the compressed air at last enters *h*, thereby lowering the pressure in *b* and the float *f* descends and opens the air outlet, the air inlet being shut.

Pulsometers built on the plan of the Pohle air-lift for wells are favored by some concerns where the necessary depth of well can be obtained readily. These lifts supply a

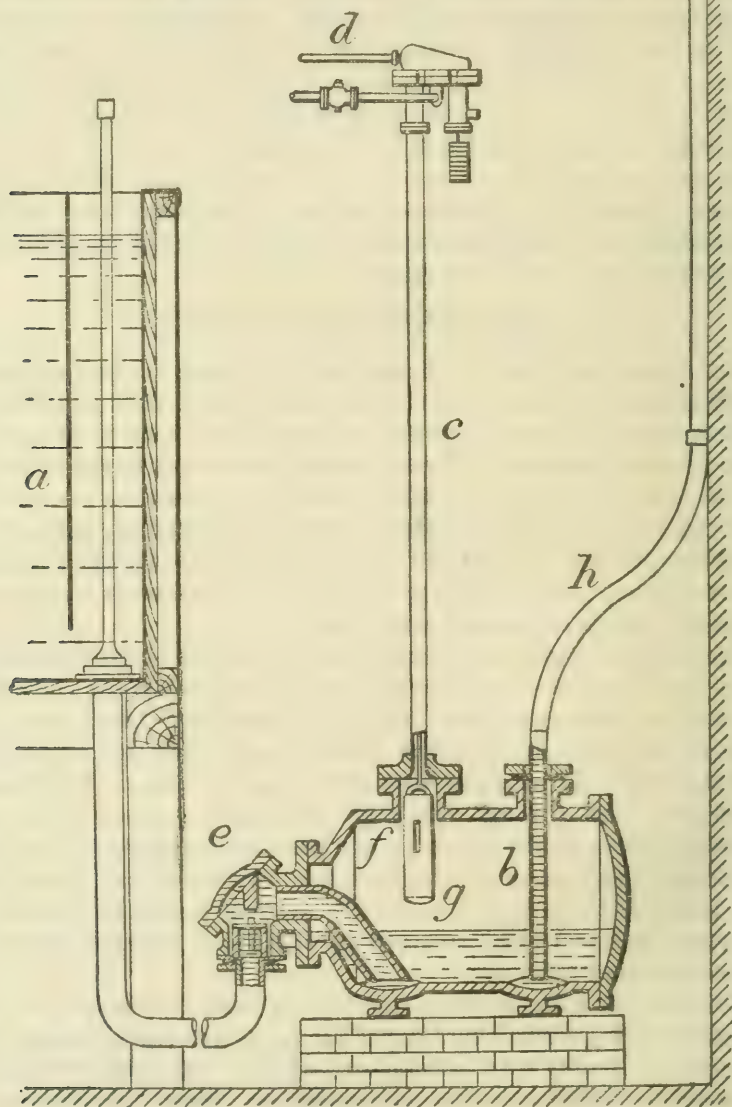
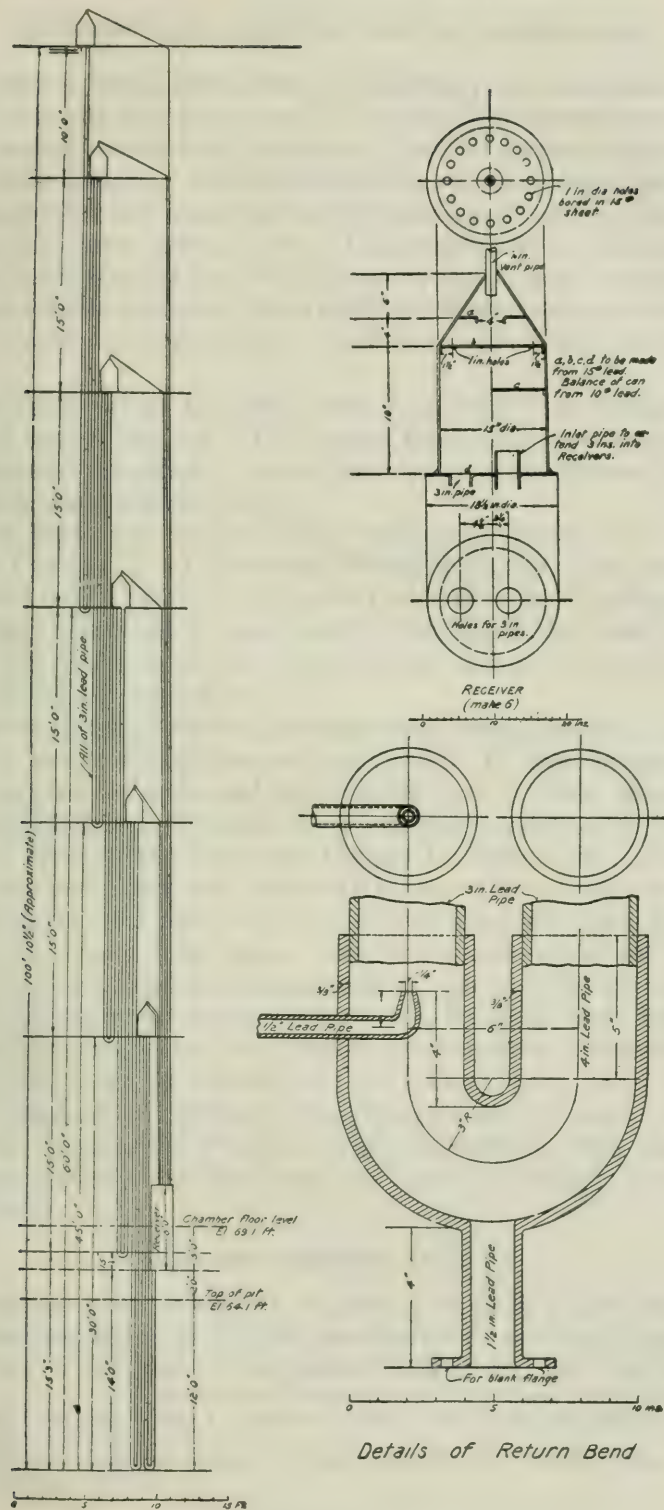


FIGURE 13.—Kestner acid pump.



POHLE MULTIPLE-STAGE AIR LIFT.

steady stream like a pump, have no moving parts, and thus can be made practically free from wear. The control of the amount of acid being pumped is reasonably accurate. Plate XI shows an adaptation of the Pohle air lift.^a The acid is lifted in stages through lead pipes, the distance between successive receivers being 15 feet, and the total lift in each column being 45 feet. The compressed air is introduced by a jet just above the bend of the pipes, the acid flowing by gravity from the receiver and being lifted by the air to the next receiver above. The lift has a pumping capacity of 300 tons to 500 tons of acid per 24 hours.

Centrifugal pumps of special cast iron have been utilized with excellent success for low lifts, among these being antimonial-lead closed-runner centrifugal pumps, lead-lined closed-runner centrifugal pumps, and duriron pumps.

A new acid-proof pump is now being manufactured by G. H. Elmore, Colonial Trust Building, Philadelphia, Pa. The materials being used in the pump are acid-proof stoneware and "bario metal," an extremely hard alloy, upon which it is claimed the acids have no effect. The pump is of the open-impeller, side-suction type, made either for belt or motor drive.

Heavy-walled lead pipe is generally used throughout the chamber plant for the transportation of weak acid. In some plants lead-lined iron pipe has been used, also special types of iron, such as corosiron, duriron, and tantiron. Cast iron can be used for 60° B. acid.

At the plant of the Tennessee Copper Co., where the amount of acid in circulation per day is over 3,600 tons, after various means of circulating the acid had been tried it was concluded that although other devices may have lower costs for power consumed yet as regards efficiency, operating labor required per unit of acid pumped, cost of repairs, total operating cost, and freedom from interruptions, no elevating device has equaled the compressed-air blow case.^b At that plant, with the exception of the chamber acid, for which the air lift is used, all acid lifting is done by means of blow cases. All the blow cases are made of riveted wrought-iron plates. The feed and discharge lines of these blow cases are 6-inch and 4-inch iron pipes, respectively.

COST OF CHAMBER PLANT.

The cost of construction of a chamber acid-plant prior to the war varied between \$2,000 and \$3,000 per ton, 60 B. acid, daily capacity, depending on the size of the plant, its location, and the general

^a De Kalb, Courtenay, Calumet & Arizona sulphuric acid plant: Min. and Sci. Press, Mar. 30, 1918, vol. 116, p. 444.

^b Fairlie, A. M., Large-scale sulphuric acid manufacture: Chem. and Met. Eng., vol. 19, Sept. 25, 1918, pp. 404-408.

local conditions for building. During 1917 and 1918, the cost increased to about \$4,000 per ton capacity, not including the roasting and burner equipment. Thus a plant of about 100 tons capacity, 60° B. basis, is estimated to cost at the present time about \$500,000, including the roasters or sulphur burners, bins, and storage tanks, etc. The same plant in 1914 would have cost about \$300,000.

COST OF MANUFACTURE OF CHAMBER ACID.

The cost of manufacturing sulphuric acid by the chamber process, of course, varies greatly according to the cost of raw materials—pyrite, sulphur, or waste gases, and sodium nitrate—the efficiency and skill of operation, and to a considerable extent the design and the construction of the plant, as it may be or not be well designed for the most economical operation.

At one large well-designed plant, exclusive of plant amortization charges, or cost of sulphur-bearing material, but including cost of roasting, and all charges for operation and repairs, labor and materials, the cost of producing 50° B. acid under 1914 conditions was not more than \$2 per ton. With sulphur-bearing material at 15 cents per unit of sulphur, the total cost, exclusive of amortization charges, would be about \$5 to \$5.25 per ton of acid (50° B. basis).

The cost of concentrating chamber acid to 60° B. strength was very small, as the plant was well designed, having ample Glover tower capacity and sufficient heat in the gases for the purpose, and thus the cost of producing 60° B. acid was about \$2.60. With sulphur at 15 cents per unit, this makes a total cost of about \$6.75 per ton of 60° B. acid.

During the latter part of 1918, when the cost of sulphur was more nearly 30 cents per unit at acid plants and the price of labor and supplies had gone up considerably, the cost of manufacturing chamber acid (60° B. basis) at the above plant had increased to about \$13.50 per ton, of which \$8.30 was for sulphur and \$5.20 was for sodium nitrate, operating labor, repairs, and supplies and general plant overhead, but not including amortization and depreciation.

The cost of raw material (sulphur gases) at plants making acid as a by-product from roasting zinc ores is much smaller than at plants operating on pyrite or sulphur, being in some instances practically nothing, but the operating cost is usually higher, as the gas concentrations are more variable, resulting in loss of nitrate of soda and greater wear and tear on the chambers. By-product acid from zinc ore has been made for less than \$4 per ton (60° B. basis) under pre-war conditions.

At a large acid plant in the west where concentrates are being roasted for the sulphur at the acid plant and then returned to the smelter for smelting, the cost of producing 60° B. acid in 1916 was between \$2.50 and \$3 per ton, of which about \$1 was the cost of roasting. By 1918 the cost had been raised to over \$5 per ton.

At the present time a plant producing 60° B. acid for \$4 per ton from pyrite, exclusive of the cost of pyrite or of plant amortization and depreciation, is doing very good work. With brimstone the manufacturing cost is somewhat less, and a \$3 cost is quite possible.

Thus, with pyrite at 15 cents per unit or brimstone at 18 or 19 cents per unit, the cost of manufacturing acid (60° B. basis) at a plant of at least 100 tons per day capacity will be about \$8 to \$9 per ton. The following example shows the estimated cost of manufacturing acid (60° B. basis) at a 100-ton plant, with brimstone at 18 cents per unit and nitrate of soda at \$4 per 100 pounds.

Cost per ton of acid.

28 units of S at \$0.18-----	\$5.05
Nitrate of soda, 3.6 per cent, equals 20 pounds-----	.80
Operating, labor, and power-----	.80
Repairs and supplies-----	.70
Overhead supervision, insurance, etc-----	.65
	8.00

PRODUCTION OF SULPHURIC ACID FROM WASTE GASES AT COPPER BLAST FURNACES.

The production of sulphuric acid from waste gases at copper blast furnaces, as practiced at the plants of the Tennessee Copper Co. and the Ducktown Copper, Sulphur & Iron Co., presents so many unusual features as compared with the ordinary methods of manufacture that a brief outline of the practice at these two smelters may well be given here.

Sulphuric acid may be manufactured from the waste gases from blast furnaces only where pyritic or nearly pyritic smelting is practiced. Without describing in detail the practice of pyrite smelting, it may be stated that this method of smelting involves the utilization as completely as practicable, as fuel for the smelting process, of the sulphur and iron contained in the ore. In true pyritic smelting no carbonaceous fuel is used. However, the term has been used to cover those cases where the percentage of coke used in the charge is less than 6 per cent, this coke being added either because the sulphur and iron content of the charge is insufficient to provide heat for the smelting process, or because it is impossible to utilize all the sulphur

and iron efficiently. The use of coke in smelting, of course, causes the presence of carbon dioxide in the exit gases, and the amount of carbon or coke that may be used in the charge if sulphuric acid is to be made from the gases is limited by the relative amounts of sulphur dioxide and carbon dioxide which will be made. Too high a coke content, such as 6 per cent or more, will produce a gas so high in carbon dioxide that the sulphur dioxide content will be too low for acid manufacture, especially when the sulphur dioxide concentration is still further diluted by air to give the necessary oxygen for carrying on the process.

The factors concerning the proper proportions of carbon, sulphur, and iron for proper metallurgical results, and the effect of variations in these constituents, or in the composition of the gases, are discussed in detail in an article by Falding and Channing.^a

If only sufficient air is blown into the furnace to provide oxygen for oxidizing the sulphur, iron, and other oxidizable constituents of the charge and no coke is used, then the exit gases will consist of sulphur dioxide and nitrogen, or, if coke is used, the gases will carry carbon dioxide with the sulphur dioxide and nitrogen. As the best metallurgical results are obtained when very little or no excess air is blown into the furnace through the tuyères, there being an exact equilibrium between the oxygen supplied through the tuyères and the oxidizable content of the charge, the exit gases under perfect metallurgical operation will contain no free oxygen.

For many reasons it is technically impossible to maintain this equilibrium; consequently the composition of the gases issuing from the furnace is irregular and fluctuates greatly. Some of the conditions tending to upset this balance are enumerated as follows:

(1) There are always unavoidable fluctuations in the charge, even when the ores are bedded and carefully mixed. (2) Irregularities in weighing are apt to exist. (3) The charging of the furnace is intermittent, with the result that for a period immediately after the charge has been dropped there is present in the furnace more sulphur, iron, and coke than is present just before charging. With an excess of oxidizable material present some sulphur may volatilize, and carbon monoxide form. (4) Occasionally blowholes form and permit air to escape from the furnace without acting on the iron, sulphur, or coke, resulting in the presence of free oxygen in the exit gases. When the metallurgical functions of the furnace are at their best, as when the smelting is going on smoothly, charges are being carefully prepared and weighed and are being fed regularly, no blowholes or furnace crusts are present, and the gases are rising

^a Falding, F. J., and Channing, J. P., Pyrite smelting and sulphuric acid manufacture: Eng. and Min. Jour., Sept. 17, 1910, vol. 90, pp. 555-558.

everly through the furnace charge. Then there is practically no free oxygen and no carbon monoxide present in the gases.

When several furnaces are in operation, discharging into a common flue, it is much easier to maintain a gas production of suitable concentration and uniformity for making acid than with only one furnace in operation.

A general misapprehension relative to the production of sulphuric acid from blast-furnace gases is that the sulphur costs nothing. This is hardly true. The operation of a blast furnace, or blast furnaces, in connection with an acid plant involves certain items of expense which would not be incurred if control of the composition of the gases as they pass into the flues were unnecessary. Of course, the extra care demanded in the management of the furnaces is, to a large extent, repaid by the better metallurgical results obtained with the furnace. However, the cost of manufacturing acid from smelter gases is higher than from gases derived from burning pyrite or brimstone. On account of the fluctuating composition of the gases, when using blast-furnace gases, it is almost impossible to realize as high an efficiency of the niter. By careful supervision and frequent and regular analyses of the gases, it has been found possible to reduce the niter consumption to a figure much lower than was obtained when plants were first operated on blast-furnace gases, but even under this careful technical supervision the niter consumption is between 6 and 8 per cent as against 3 or 4 per cent in most commercial burner plants. Furthermore, in order to obtain this result it is necessary to provide unusually large Gay-Lussac tower capacity. In the usual burner plant a Gay-Lussac tower capacity, equal to 2 or 3 per cent of the chamber capacity, is adequate for recovering 85 to 90 per cent of the niter, but in plants using blast-furnace gases it is necessary to provide at least 6 per cent. The presence of such a large percentage of CO_2 in the gases also increases the chamber space necessary for the conversion of a definite weight of sulphur dioxide, above that required in a commercial plant, and thus the interest, depreciation, and maintenance charges per ton of acid produced are greater.

PLANTS AT COPPERHILL AND ISABELLA, TENN.

The ores treated at the plants of the Tennessee Copper Co. and the Ducktown Copper, Sulphur & Iron Co. at Copperhill and Isabella, Tenn., consist essentially of pyrrhotite with only a small proportion of pyrite. The copper mineral present is chalcopyrite. The ores also carry about 4 per cent zinc blende. The gangue material consists of silicates, calcite, dolomite, and some magnetite.

A typical ore at the plant of the Ducktown Copper, Sulphur & Iron Co. would analyze as follows:^a

Mineral analysis.

	Per cent.
Pyrrhotite -----	29.50
Pyrite -----	5.82
Chalcopyrite -----	7.89
Blende -----	4.23
Magnetite -----	7.73
Quartz -----	15.59
Silicates -----	22.74
Calcite -----	2.16
Dolomite -----	3.56

Qualitative analysis.

Copper (Cu) -----	2.74
Iron (Fe) -----	30.87
Sulphur (S) -----	18.87
Silica (SiO ₂) -----	26.96
Lime (CaO) -----	1.67
Magnesia (MgO) -----	2.97
Manganese (Mn) -----	2.80
Alumina (Al ₂ O ₃) -----	2.91

The ores smelted by the Tennessee Copper Co. in 1917 analyzed about as follows:

Composition of ore smelted by Tennessee Copper Co.

	Per cent.
Copper (Cu) -----	1.5 to 2.5
Sulphur (S) -----	19.0 to 30.0
Iron (Fe) -----	23.0 to 38.0
Silica (SiO ₂) -----	14.0 to 30.0
Calcium (Ca) -----	4.0 to 5.5
Magnesia (MgO) -----	1.2 to 2.4
Alumina (Al ₂ O ₃) -----	3.5 to 4.6

Of the two plants that of the Tennessee Copper Co. is the larger. At this plant the ore is smelted in furnaces measuring 258 inches by 56 inches at the tuyère level, each handling about 400 tons daily, with a coke consumption ranging between 4 and 6 per cent. There are four of these furnaces installed, but not more than three are operated at one time.

About 85 to 87 per cent of the total sulphur in the charge is oxidized to sulphur dioxide, the rest going into the matte. On account of gas leakage from the furnace tops and of other losses, the proportion of sulphur actually utilized in the acid is only about 65 to 70 per cent of the total, or between 75 and 80 per cent of the sulphur oxidized. The gases issuing from the top of the charge, under good conditions of furnace operation, average about 8 to 9 per cent SO₂,

^a Larison, E. L., Sulphuric acid from copper smelting gases: Eng. and Min. Jour., vol. 102, Dec. 30, 1916, pp. 1121-1125.

6 to 7 per cent CO_2 , and less than 1 per cent CO , the difference being nitrogen. As these gases contain no oxygen, it is necessary to admit air enough to carry on the acid-making process and to provide some oxygen in the exit gases. This necessary air is admitted at several points in the system by a low-pressure blast. If the tops of the furnace were operated under suction, of course there would be plenty of oxygen drawn in; but as suction affords little control of air admission, it is best to make the furnace top as nearly air-tight as possible to maintain as nearly neutral a draft condition as possible in the furnace above the charge and to provide the necessary air by a positive blower. However, it is a difficult matter to adjust the draft at the furnace tops to maintain nearly neutral conditions, and there is usually some leakage of "false air" into the flues, or a back pressure, making working conditions on the charging floor of the furnace rather disagreeable. Air is blown in at the flue between the furnace and the Glover towers, and each chamber is fitted with air lines and valves for regulating the admission of air, so that an oxygen content of between 3 and 4 per cent is maintained throughout the system.

In the first installation at Copperhill the chambers were built along the lines of Falding's theories, some of the chambers being 77 feet high. In all there were 34 chambers, having a total capacity of about 4,000,000 cubic feet. Subsequently a second plant with four huge chambers, having a total chamber space of 2,228,000 cubic feet, was erected, making the total chamber space for the plant more than 6,000,000 cubic feet. During the war the plant produced as much as 1,000 tons of acid (50° B. basis) per day. The original installation has been described in detail by Stevens^a and Nelson^b and the recent improvements by Fairlie.^c

The plant of the Ducktown Copper, Sulphur & Iron Co.^d was built more along conventional lines. There were 16 chambers, each 24 by 96 feet by 3 feet high, connected eight to a set, with special flue connections designed to mix thoroughly and cool the gases and to prevent segregation of carbon dioxide.

This plant has been operated from one blast furnace for long periods. A novel temperature-controlling device in use in connection with the dust-cleaning system seems to overcome some of the difficulties incident to operating a plant from a single blast furnace.

^a Stevens, H. J., *Copper hand book*, Tennessee Copper Co., Tenn.: vol. 10, 1910-11, pp. 1661-1667.

^b Nelson, W. A., *Manufacture of sulphuric acid in Tennessee for 1911: Resources of Tennessee*, Tennessee Geol. Survey, vol. 2, 1912, pp. 23-24.

^c Fairlie, A. M., *Large-scale sulphuric acid manufacture*, Chem. and Met. Eng., vol. 19, Sept. 25, 1918, p. 404.

^d For detailed description of this plant, see "Smeltery smokes as a source of sulphuric acid." by W. H. Freeland and C. W. Renwick, Eng. and Min. Jour., vol. 89, May 28, 1910, pp. 1116-1120.

One of the adverse factors in the manufacture of acid at these plants is the presence of zinc oxide and sulphates in a very finely divided impalpable fume carried along by the gases. This fume does not settle out readily in the dust chambers, but is carried over into the Glover towers and into the acid chambers, tending to clog the gas passages and flues, contaminate the acid, and clog the circulating pumps. In order to remove as much of the zinc fume as possible, special dust-collecting devices, or chambers, containing baffles or channel irons to aid precipitation by offering contact surfaces, have been installed. Metallic zinc is now being recovered from the fume. In spite of these devices, however, some zinc fume goes through into the chambers, and the "front-chamber" acid produced by these plants at times is "dirty" or "sludgy." A large proportion of the product has satisfactory clearness and purity.

PURIFICATION OF CHAMBER ACID.

With the exception of lead sulphate, nearly all the impurities of chamber acid are brought into the system by the burner gases, and the character and amount of such impurities depend largely upon the kind of raw material being used.

The impurities consist of various oxides of arsenic, antimony, selenium, lead, iron, zinc, copper, lime, aluminum, fluorine, together with nitrous and nitric acid, nitric oxide, and organic matter.

Most of the impurities not collected in the dust chambers are mechanically deposited as sediment in the Glover towers, or in the first chamber. Even when the "first-chamber" acid is dirty it is usually possible to obtain from the back chambers a sufficiently pure acid for most manufacturing purposes. At most phosphate fertilizer plants, the presence of impurities in the proportions usually found is not important and no attempt is made to purify the acid.

The nitrous compounds are removed by heating the acid with 0.1 to 0.5 per cent of powdered ammonium sulphate present.

Most acid plants making acid for precise manufacturing purposes exercise great care in the selection of pyrite and have effective dust-collecting systems, or use brimstone, so that the amount of impurities getting into the acid is very small.

However, at some plants where there is a decided advantage, as regards costs of production, in using waste gases from desulphurizing impure sulphides, especially zinc blende and arsenical copper sulphates, it is desirable to purify part or all of the output of acid.

When the impurities are solid particles held in suspension, it is usually possible to clarify the acid by allowing it to stand in settling chambers and then siphon or pump the clear acid from above the

settled material. Some impurities remain in solution and require chemical treatment. The most troublesome of all are arsenic and selenium. The latter can be precipitated by the addition of a small quantity of potassium chloride. Arsenic is present usually in much larger quantities, the content varying up to even 0.5 per cent, and unless practically eliminated will contaminate all products manufactured from the acid. Thus, with the stringent requirements of the pure food and drug act, the dearsenication of sulphuric acid is important. Arsenic is removed by the use of hydrogen sulphide (H_2S). Three types of apparatus are used for the purpose, as follows:

1. The old type of tower in which the H_2S gas ascends a lead-lined tower, specially packed, and meets a downward stream of weak chamber acid. This method is costly, wasteful of H_2S , and requires considerable dilution of the acid.

2. The intermittent method, using closed vessels and blowing H_2S gas into the vessel under pressure. This method permits precipitation of the arsenic from acid of fairly high strength and therefore saves subsequent concentration. It requires a considerable excess of H_2S .

3. The modern "Trepex" machine is continuous in operation, the raw acid being agitated by revolving propellers or paddles and coming into intimate contact with the H_2S gas. The agitation also prevents settling of the arsenic sulphide. A "Trepex" machine consists of an iron drum, which is divided into sections. The drum is lined with a special enamel that is very resistant to acid up to 200°C . Vents in each section are so placed that the sulphuric acid runs from one section to another until it reaches the outlet pipe, thence it goes to a settler or to a filter tank, where the arsenic sulphide is completely filtered out. The filter tanks usually have false bottoms with a grid composed of heavy plank and covered with lead or acid-proof brick, having communicating gutters underneath. The grid is covered with pieces of quartz and then with finer material. The upper layers are ordinary sand over which a perforated lead sheet is placed to prevent disturbing the arsenic sulphide when the filter is cleaned. The filtering layer thus formed is finally covered with a layer of dry arsenic sulphide. For light arsenical ores the porous type of filter is in considerable use. This filter is composed of porous tiles, jointed by suitable mortar (such as silicate of soda and water thickened with "lava" or "volvic" stone).

The excess of hydrogen sulphide from the machine is either absorbed by caustic soda solution or milk of lime. The hydrogen sulphide is generated by treating ferrous sulphide with warm dilute acid (20 to 40 per cent H_2SO_4) in a suitable generator constructed similar to an ordinary Kipp generator.

The dearsenicators range in size from 20 to 500 ton capacity weekly. The advantages of the Trepex machine over the other forms of dearsenicators are (1) small initial expense and small operating cost, (2) effective use of H_2S and practically complete elimination of arsenic compounds, and (3) large continuous output at low cost.

The Trepex machine was developed by the Davis Bros., Manchester, England, and was introduced into this country by the Industrial Research Corporation, New York City.

For the precipitation of arsenic in the Trepex machine, the acid must be diluted to about 65 per cent or 53° B. The purified acid can not be reconcentrated by evaporation in the Glover towers, as it would be again contaminated by the impurities in that tower. Thus, whenever acid is to be purified the usual procedure is to take the acid directly from the chambers, and then after purification to concentrate the acid in special types of concentrators.

As this operation is of minor importance, or not practiced at all at most plants in this country, further discussion will not be given here. An excellent description of the management and control of a plant for the dearsenication of sulphuric acid is given by Cory.^a

One method of removing arsenic from acid is by precipitation with barium sulphide. This method, however, is rarely used. Its advantages are that (1) the barium is itself precipitated as sulphate and thus adds greatly to the weight and density of the precipitate, and (2) all other soluble material is precipitated. To precipitate with barium sulphide, however, the acid must be diluted to 50 per cent strength, and then heated to 80° C.

With the removal of the arsenic by either the H_2S or BaS precipitant, practically all other impurities except iron and aluminum are removed at the same time and the acid is even clarified from inert suspended matter.

At new chamber plants, uncontaminated by impurities from pyrite, etc., it is possible to make clear acid by the use of brimstone; but to produce a thoroughly pure clear white acid from impure pyrite or other impure materials it is necessary to use a distillation method of purification or to make acid by the contact process.

CONCENTRATION OF CHAMBER ACID TO 60° B. STRENGTH.

Attention has already been called to the fact that with the proper use of the Glover tower the whole output of chamber acids can be concentrated from 50° B. to 60° or 62° B. The chief advantages of this system over any other method of concentration are that (1) the

^a Cory, H. E. J., Dearsenication of sulphuric acid. *Scientific management and control: Chem. Trade Jour. and Chem. Engineer*, vol. 62, Feb. 2, 1918, pp. 89-90.

heat of the combustion of the pyrite or brimstone is utilized for the purpose rather than expensive fuel. (2) the steam thereby produced is returned to the system where needed in the lead chambers, and (3) all weak acid distillates are returned to the system without loss or additional cost for concentration.

The only drawback to this method is the impurity of the acid when produced at plants burning pyrite or other metallic sulphides.

For concentrating chamber acid directly to 60° B., or for reconcentrating purified acid to 60° B., evaporation has been effected in leaden pan evaporators, heated either by a direct fire, by steam, or by waste heat from the pyrite burners. In some installations the hot gases passed directly over the pans and in others the pans were heated from the bottom. The first method produces the most rapid rate of evaporation, but is not employed when clear acid is desired, as the hot gases are apt to leave dust or soot on the surface of the acid. Various forms of lead-pan evaporators, with various methods of firing, have been used in the past for the concentration of acid to 60° B., but as the method is seldom used in this country now and the tonnage of acid concentrated in this way is comparatively small, further discussion will not be given here. Details of lead-pan evaporation of acid to 60° B. are given by Lunge.^a

CONCENTRATION OF SULPHURIC ACID TO 66° B. STRENGTH BY HEAT.

Although commercial "oil of vitriol" (66° B. acid) can now be made more cheaply by the contact process than by the heat concentration of chamber acid or of 60° B. acid, yet in certain plants in this country this higher-strength acid is being made by the concentration of the weaker acids. During the war, when the demand for higher-strength acid was great and the price was high, concentrators were put in and utilized at various plants. With the end of the war, many of these concentrating plants have been shut down. However, as a certain amount of 66° B. acid is now being produced and for various reasons will continue to be produced by the heat concentration of chamber acid, a description of the more modern concentrators is desirable. These concentrators are used also for concentrating waste acids or spent acids from the manufacture of explosives, dyes, and various other products in the manufacture of which sulphuric acid is used as a dehydrating agent. A small amount of acid has been concentrated to 98 per cent strength by heat concentration, but if strengths higher than 95 per cent are required it is much more economical to bring up the strength of 66° B. acid (93.18 per cent H_2SO_4) by adding fuming acid or oleum.

^a Lunge, George, Sulphuric acid and alkali, vol. 1, pt. 3, 1913, pp. 1079-1193.

Sulphuric acid can be concentrated by evaporation up to 98.3 per cent H_2SO_4 , at which concentration it possesses its highest boiling point, 338°C ., and can be distilled without decomposition. Acid of higher strength than this decomposes under heat and gives SO_2 , H_2O , and O .

CONCENTRATION IN STILLS.

Formerly considerable acid was concentrated in stills heated externally by waste gases or by coal fire. These stills were made of glass, porcelain, or platinum, and finally of special cast iron. Glass and porcelain stills were early discarded because of the heavy breakage involved. Large quantities of acid have been evaporated in former years in platinum stills, but as the cost of platinum became greater and greater, the cost of these stills became prohibitive. Furthermore, the hydrogen, carbon, sulphur, and silica present in the heating gases cause deterioration of the platinum, and various impurities in the acid also cause slight chemical reactions, so that the cost of maintenance became increasingly greater as the cost of platinum rose.

Cast-iron stills have been used successively for the higher concentration of acid, that is, from 66°B . (93.18 per cent) even to 98 per cent. Below 66°B . the action of acid on ordinary cast iron is very severe and the life of a still was usually less than three or four months. Special grades of cast iron high in silicon are now made—namely, corosiron, duriron, and tantiron—which have a greater resistance to such strength of acid, and pans of these special irons are now successfully employed as concentrating stills.

In one modern installation the stills were of duriron, were kettle-shaped, about 4 feet in diameter and 2 feet deep, with flat tops to allow setting them in the brick walls so as to be almost entirely surrounded by fire space. Tops were provided for these stills to lead the vapors to a condenser of lead.

Cast-iron stills are built in various shapes.^a In some types provision is made for cascading the acid through several shallow stills, each being provided with partitions to force the acid to travel in zigzag manner and thereby expose it to the heat more efficiently.

The greatest cause for deterioration of the still is by the formation of a "scale" or deposit of ferric sulphate on the bottom. This scale not only decreases the efficiency of the still, but causes local overheating of the iron beneath the "scale" and subsequent burning or cracking. Thus, provision must be made for cleaning the stills either through a "mud drum" in the bottom or by access to the still from above.

^a Lunge, George, *Sulphuric acid and alkali*, vol. 1, 1913, pt. 3, pp. 1158-1179.

More fuel is required for the concentration of acid in cast iron than in platinum. As against a coal consumption of approximately 20 per cent in platinum stills, the consumption of coal in concentrating acid from 60 to 66° B. in cast-iron pans is about 30 per cent.

Kessler's still, described by Lunge^a and by Rogers,^b in which concentration was effected by the heat from a coke fire or producer gas, was tried in this country about 1900, but its use has not been general. From the Kessler still has been developed the modern tower concentrator which is described on subsequent pages (pp. 139).

With the advent of successful modern tower concentrators the use of the cast-iron stills has become less and less important.

CONTINUOUS CASCADE CONCENTRATORS.

The continuous cascade concentrator was originated in England, and at first consisted of four or five glass retorts arranged in cascade over a coal or a gas fired furnace. Porcelain dishes set in an acid-proof brick chamber were later substituted for glass retorts. One of the most serious drawbacks to this system, whether using glass or porcelain, was the heavy breakage of the pans and the difficulty of getting high fuel efficiency; hence the system was not generally adopted.

With the development of vitreosil (fused silica) in 1906, there was a more general adoption of the use of cascade systems, and several were installed in this country. The largest is at the plant of the Davison Chemical Co., at Baltimore, Md.

An elevation of a concentrating plant with the cascade system^c is given in figure 14.

The upper pans are 24 inches by 12 inches, and the dishes are 12½ inches in diameter. In a unit to produce 10 tons of 66° B. acid per 24 hours from 50° B. acid, there would be 60 preheating pans and 100 dishes, the pans arranged in six rows of ten pans each, and the dishes in four rows of 25 dishes each. All the pans and dishes, except the last three dishes in each row at the lower end of the system, are supported in open seats and are directly exposed to the fire gases. The last three dishes have closed seats in order to provide protection to the seating from the boiling and spurting of the acid in the dishes. Natural-draft furnaces burning soft coal are in general use, the fuel consumption being about 17 per cent, based on the weight of the finished product. Breakage of the dishes amounts to about 5 per cent, and of the pans to about 1 per cent per annum. Vitreosil

^a Lunge, George, *Sulphuric acid and alkali*, vol. 1, pt. 3, 1913, pp. 1142-1149.

^b Rogers, Allen, and Aubert, A. B., *Industrial chemistry*, 2d edition, 1915, Chap. I, General process and materials, pp. 1-31.

^c Marshall, A. E., *Fused silica dishes for the concentration of sulphuric acid*: *Met. and Chem. Eng.*, vol. 13, Mar., 1915, pp. 136-137.

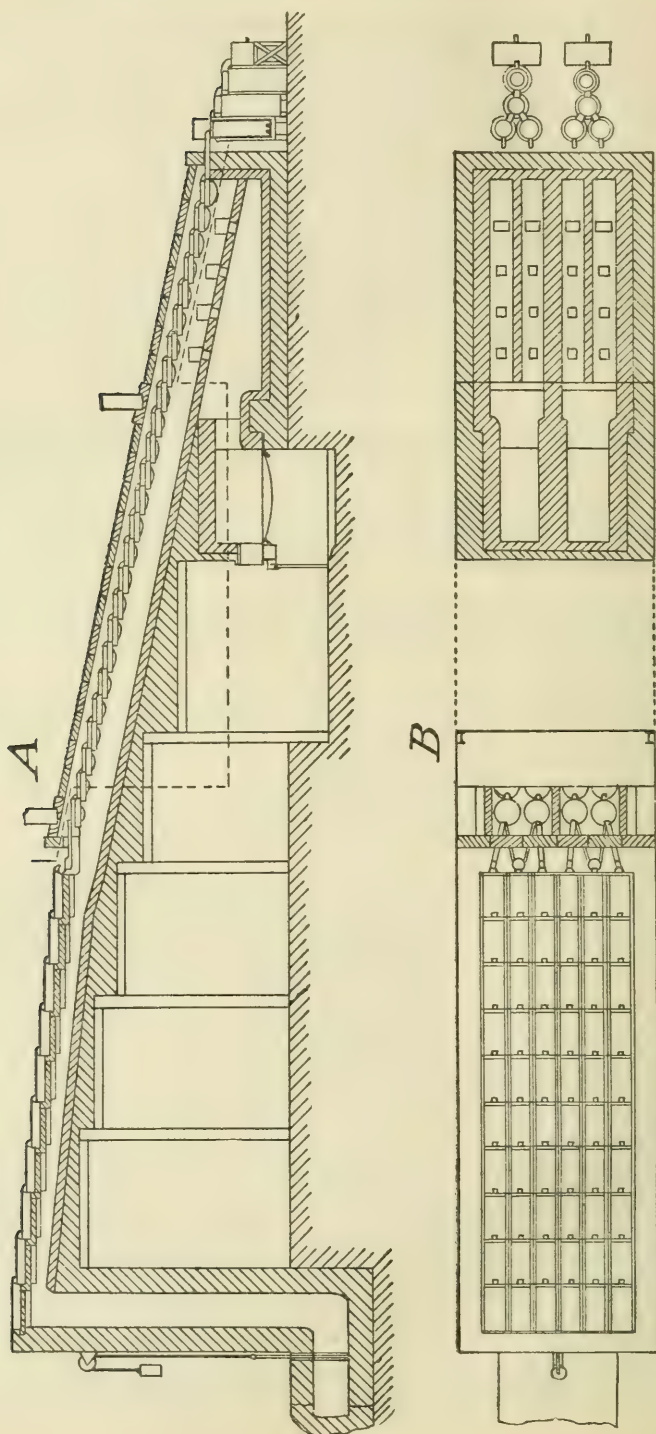


FIGURE 14.—Cascade system of concentration. A, elevation; B, plan.

has a very low coefficient of expansion, about one-sixth of that of porcelain. Thus vitreosil dishes do not break through temperature changes, no matter how severe. This resistance to temperature changes permits the vitreosil dishes to be directly exposed to the fire gases in open seatings, thus permitting higher fuel economy than when the dishes must be protected from the direct flame by slabs or other means.

With this type of concentrator the loss of acid fume or mist is relatively very high unless apparatus for the recovery of the fume are installed. Coke towers have usually been installed for the purpose until the advent of electrical precipitation. These are described later.

The cost of concentrating with this type of concentrator in a 10-ton unit is about as follows per ton of 66° B. acid from 60° B. acid:

Coal, 17 per cent, at \$5 per ton.....	\$0. 85
Labor.....	1. 25
General expense and repair.....	1. 00
Losses, 4 per cent of acid, assuming 60° B. acid=\$8 per ton.....	. 30
Total, per ton of 66° B. acid.....	3. 40

Cascade systems may be made having pans made of alloys of iron, such as duriron, tantiron, and corrosiron. These pans may be open and provided with lips for the acid to cascade from each basin to the lower one ahead and becoming more and more concentrated in each basin. These can be placed in a flue with acid brick setting and heated from below as in the operation of vitreosil pans.

CHEMICO CONCENTRATOR OF THE CHEMICAL CONSTRUCTION CO.

The principal apparatus of the chemico concentrator (see fig. 15), consists of a combustion chamber, a concentrating flue, concentrating tower, filter and scrubbing tower, all of which are constructed of acid-proof masonry, well braced with steel framing, and supported on concrete or brick foundations at a suitable height above the ground level. On top of the concrete foundations masonry-lined lead pans are used, on which are built the masonry walls. The concentrating tower is packed with checkered brick, quartz, or other suitable packing and the filter tower is packed with 3-inch special rings.

Fuel oil, natural gas, or producer gas is used to generate the hot gases for evaporation. These gases pass from the combustion chamber through the concentrating flue and then up through the concentrating tower, where they come in contact with the weak descending acid which is thus preheated and partly concentrated. From the top of this tower the gases are drawn at a temperature of about 220° F. and are led through a lead or stoneware flue to the top of the filter

and scrubbing towers. An exhaust fan placed at the base of the scrubbing tower draws the gases through this tower and discharges them into the atmosphere.

In flowing through the concentrating flue the gases pass over a pool of acid which is violently agitated by forcing compressed air through it from perforations in a pipe running submerged in the acid and lengthwise of the flue. Thus a large area of acid is exposed to the direct action of the hot combustion gases.

In passing up through the concentrating tower the gases come into contact with a countercurrent of weak acid. The tower is

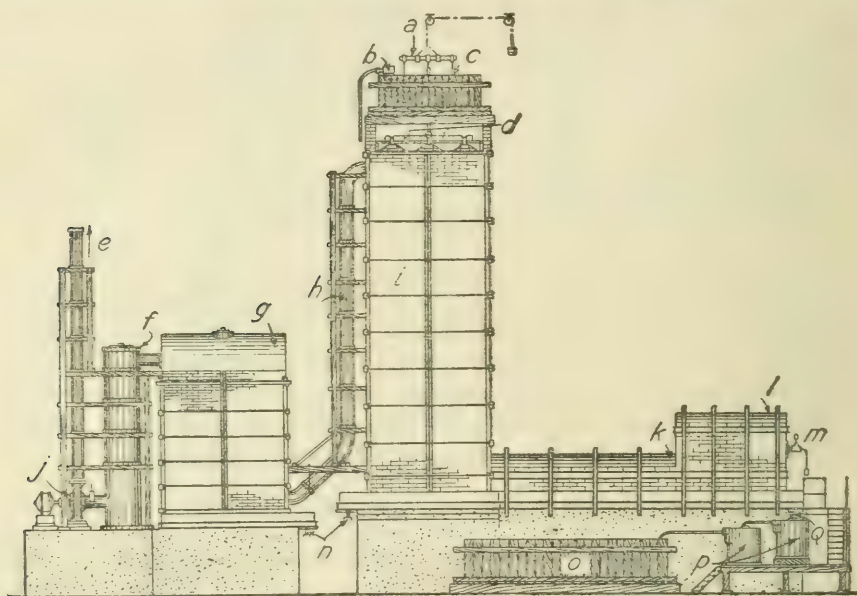


FIGURE 15.—Chemico concentrator, side elevation; *a*, Acid regulator; *b*, blow box; *c*, distributing tank; *d*, acid distributor; *e*, exit for steam and combustion gases; *f*, scrubbing tower; *g*, filter tower; *h*, gas flue; *i*, concentrating tower; *j*, exhaust fan; *k*, concentrating flue; *l*, burner; *m*, oil and gas burner; *n*, wash out and acid overflow; *o*, intermediate and storage tank; *p*, acid coolers; *q*, acid overflow.

packed to allow a large contact surface for the gas and the acid, and the first portion of the concentration takes place in this tower. The flow of weak acid to the concentrator from an overhead tank is regulated to suit the conditions and results desired. The acid flows from the distributing pan to air-sealed lutes, which are equally distributed over the tower top and distribute the acid uniformly over the upper surface of the packing.

In the filter and scrubbing towers the acid mist carried over by the waste gases from the concentrating tower is to a large extent recovered, though not entirely so. The loss may be 2 to 4 per cent of the total acid.

The hot concentrated acid from the concentrating flue is drawn off into lead coolers. All iron salts deposit in the flue and in no way interfere with the efficiency of the concentration, the iron salts being removed through suitable openings without shutting down the concentrator.

The chemico concentrator requires about 13 to 14 gallons of crude oil to concentrate 1 ton of 66° B. acid from 50° acid. As the gases are discharged at 200° F. or less and the radiation loss is relatively small, the heat is fairly well utilized. These concentrators have been built in sizes having capacities of 15 to 125 tons of 66° acid per 24 hours.

KALBPERRY CONCENTRATING TOWERS.

The original Kalbpery tower was first erected and put into operation about 1906 and has been in continuous service ever since. The towers are now built in various sizes and capacities by the Kalbpery Corporation of New York City. The standard tower is 5 feet square by 39 feet high over all, with an actual concentration height of about 25 feet. The standard tower has a capacity of 1 ton of acid per hour (60° to 66° B.). A typical arrangement is shown in figure 16.

Liquid or gaseous fuel is burned in the furnace, 1, the gases of combustion passing through the flues 1*a* and 2*e*, into and up through the tower 2, and to the scrubber 3.

The acid to be concentrated is delivered to the supply tank 2*a* and thence fed into the top of the tower by the automatic feeding apparatus 2*b*, 2*c*, whence it flows down over the packing in the tower against the rising hot gases, the concentrated acid flowing from the tower through the exit 5 and the coolers 6 and 7 into tank 9.

The acid fumes driven off in the tower and air pass through the scrubbers 3, thence through the suction fan 11, and thence through the auxiliary scrubber 4, before being exhausted to the atmosphere at 4*c*.

A so-called "5-foot" tower has a capacity for producing, when concentrating sulphuric acid from 60° B. to 66° B., about 1 ton of 66° acid per hour.

The fuel consumption will be about 10.5 to 12 gallons of 19,000 B. t. u. fuel oil per ton of 66° acid, concentrating from 60° B. to 66° B. In addition to the concentrated acid produced, about 10 per cent of the sulphuric acid charged is recovered as weak or scrubber acid of a strength of about 40° to 46° B., and there is a loss to the atmosphere of about 2 per cent.

One man can easily handle a battery of four towers.

Towers may be built of as large a capacity as is commercially desirable—they have been built with a minimum capacity of less

than 2 tons per day—and concentration may be made from chamber strength up to 96.5 or 97 per cent. the limit of concentration attainable for sulphuric acid.

SKOGLAND CONCENTRATOR.

The Skogland concentrator is built by the Pratt Engineering Co., of Atlanta and New York. The greater part of the evaporation in

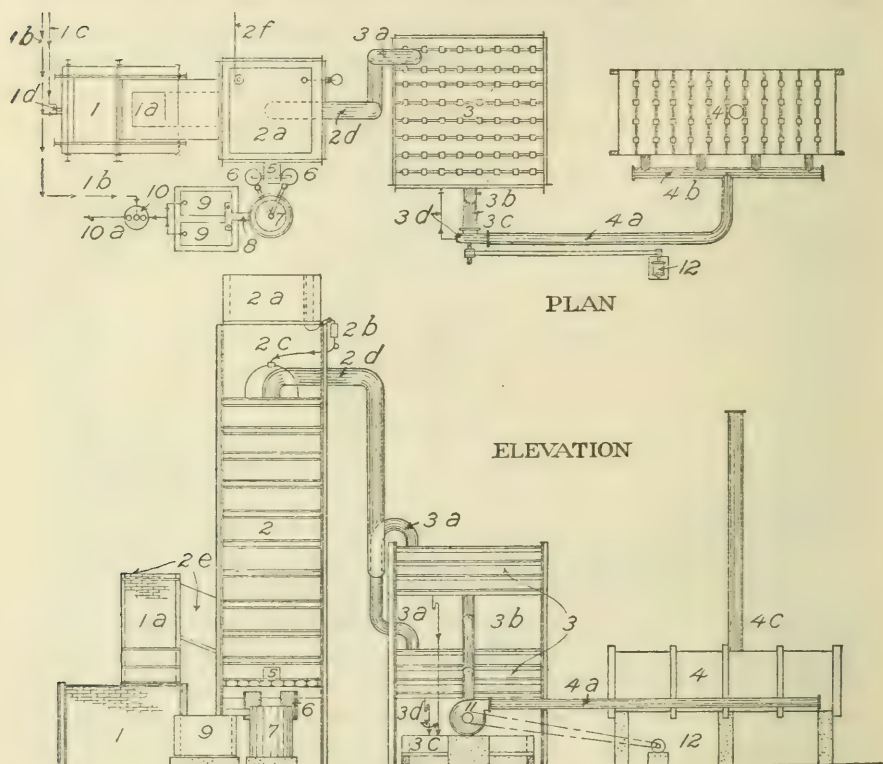
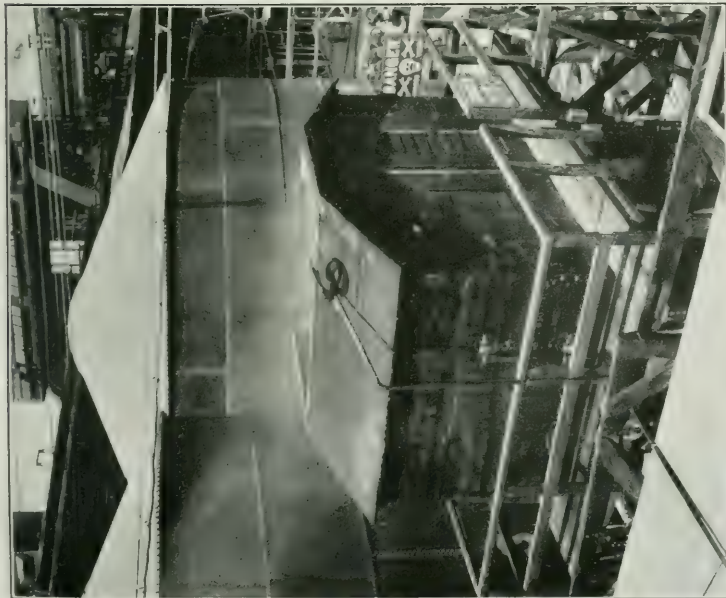


FIGURE 16.—Kalbpery concentrator, 1, 1a, 2c, Furnace and flue; 1b, 1c, 1d, air and oil piping; 2, concentrating tower; 2a, 2b, 2c, 2f, acid supply tank, siphon, and tower feed; 2d, outlet gases from tower; 3, 3a, 3b, 3c, scrubber and gas flues; 3d, 3e, scrubber acid piping and tank; 4, 4a, 4b, 4c, 4d, auxiliary scrubber and piping; 5, outlet for concentrated acid; 6, 7, acid coolers; 8, 9, concentrated-acid tank; 10, 10a, montejus; 11, fan; 12, motor.

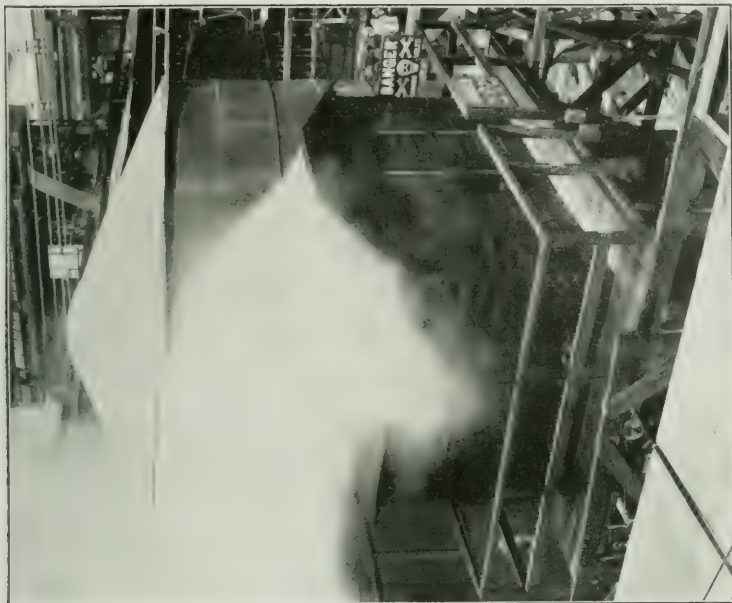
this concentrator is brought about by the spraying of the acid in a chamber through which the hot combustion gases are passing. The fuel consumption of the Skogland concentrator averages around 12 gallons of oil per ton of 66° B. acid concentrated from 50° B. acid.

ELECTRICAL CONCENTRATOR.

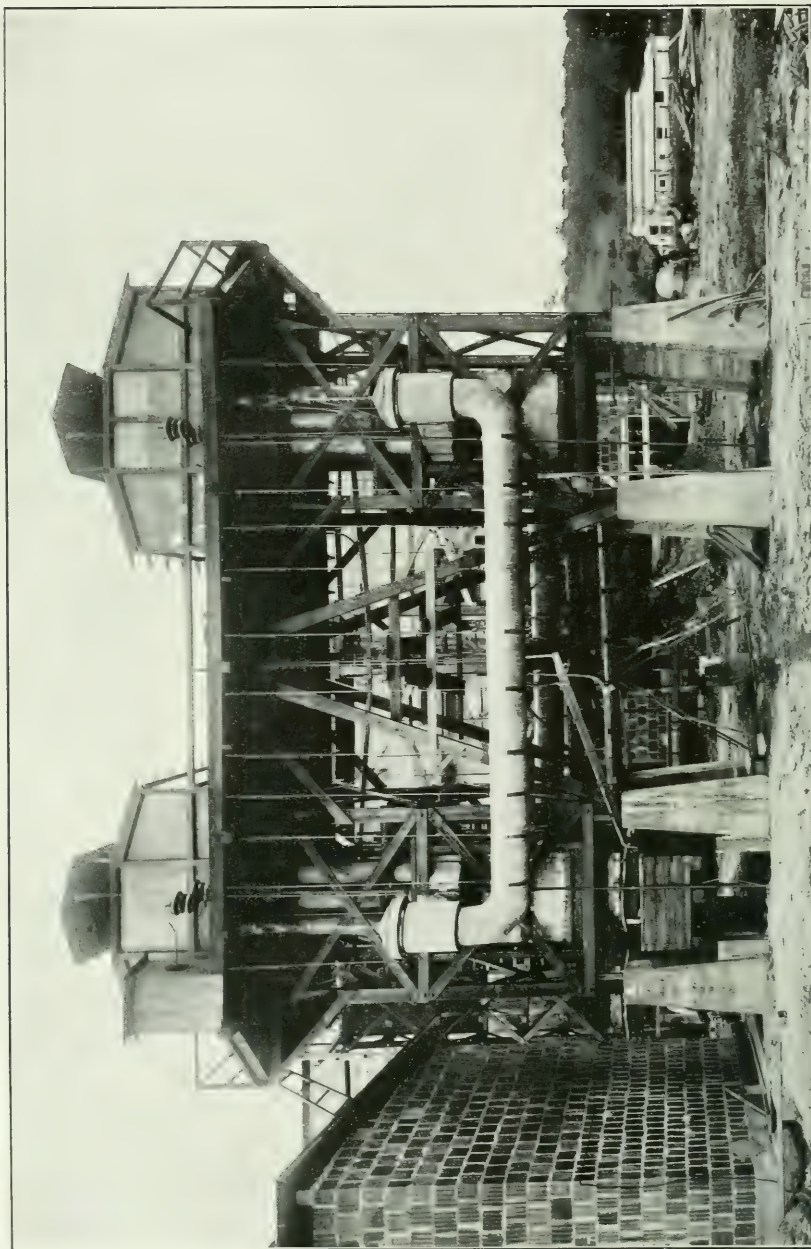
An electrical concentrator has been installed by the Chemical Construction Co. at Mount Holly, N. C., and has been operated inter-



A. ELECTRICAL PRECIPITATOR FOR SULPHURIC ACID FUMES, CURRENT ON.



B. ELECTRICAL PRECIPITATOR FOR SULPHURIC ACID FUMES, CURRENT OFF.



LARGE ELECTRICAL PRECIPITATION PLANT FOR REMOVING ACID MIST FROM GASES FROM SULPHURIC ACID CONCENTRATORS.

(By courtesy of the Research Corporation.)

mittently for several months with good results. During 1918 a 1-ton capacity unit was installed at a chemical plant at St. Albans, W. Va.

This concentrator is designed for small capacities where electrical current is available and comparatively cheap. It consists of a small bath space built of acid-proof masonry in which are placed two electrodes of acid-proof iron spaced about 2 or 3 feet apart, the electrodes being adjustable. The bath of acid is also so arranged that the level may be lowered or raised. There is a dam of acid-proof masonry between the electrodes. The weak acid is fed in at one end of the furnace near the electrode and flows over the dam to an outlet at the other end. The electric current between the electrodes passes through the thin layer of acid flowing over the dam and heats this thin layer to the point where the water is evaporated at a rapid rate.

USE OF ELECTRICAL PRECIPITATION PROCESS FOR RECOVERY OF ACID MIST OR FUME.

With most types of acid concentrators, Kalbperry towers, Skogland evaporators, or cascade systems there is always a considerable amount of acid mist or fume produced which is carried out by the furnace gases. This mist is difficult to catch completely in coke or other types of towers unless passed through weak acid or water in a scrubbing tower, when the resulting acid is so dilute that it is of little value. However, the discharge of acid mist into the atmosphere often leads to more or less serious complaints by people living adjacent to the plants and sometimes to litigation, resulting in the complainants procuring an injunction decree from the courts preventing further discharge of fumes.

The most efficient method of recovering the acid mist has been by electrical precipitation. The principle and mechanics of the process have been discussed under the subject of the recovery of dust and fume and will not be repeated here.

The precipitators used for recovering acid mist are invariably of the pipe type and the material used is, of course, acid proof. Lead is nearly always used for the top and bottom headers, while the collecting electrode may be of lead or tile.

Plate IV, *B* (p. 67) shows an electrical precipitator erected for removing the acid mist from 3,000 cubic feet of gas per minute at 135° F., coming from three sulphuric-acid concentrators producing a total of 50 tons of 66° B. acid per 24 hours. Plate XII, *A*, shows an electrical precipitator with the current on, and Plate XII, *B*, with the current off. Plate XIII shows a large installation at a chemical plant in Tennessee.

One of the largest precipitation installations now in service for the removal of acid mist arising from sulphuric acid concentrators is

one where the waste gases from 22 concentrators of the cascade type, each having a rated capacity of 10 tons of 66° B. acid per 24 hours, may be treated. The volume of gas cleared averages 30,000 cubic feet per minute at 180° F. and there is collected about 25 tons of 40° B. acid per day. The precipitator comprises four units, each having 12 collecting electrode pipes 12 inches in diameter by 15 feet in height. One set of electrical equipment of the usual type furnishes the power required by the installation.

In the following table there are listed the electrical precipitator installations that have been erected and satisfactorily operated for removing sulphuric acid mists from gases from concentrators. This table includes data on the number and type of towers with their combined capacities and feed, the recoveries and concentration of the recovered acid, and essential data on the size and operating conditions of the precipitators.

Data on removal of acid mists from concentrator gases by electrical precipitators.

Installation.	No. and type of concentrator.	Capacity, tons of 66° B. acid per 24 hours.	Strength of acid feed, °B.	Strength of acid precipitated, °B.	Tons of acid precipitated per 24 hours.	Tons of acid precipitated reduced to 66° B.	Percentage of total acid precipitated.	Number of pipes in precipitator.	Volume of gases, cubic feet per minute.	Temperature of gases, °F.	Cost of installation.
A.....	1-K	16	53	16	0.72	0.13	0.8	5	1,000	150	\$3,000
B.....	2-K	43	53	16	1.6	.3	.8	19	2,000	150	5,000
C.....	3-K	37	53	16	1.85	.35	1.0	12	2,400	150	5,000
D.....	5-K	90	50	20	15.0	3.6	4.0	32	6,000	123	14,000
E.....	3-S	50	50	18	3.3	.7	1.4	16	2,640	135	6,500
F.....	1-S	40	60	33	1.75	.7	1.8	12	2,250	206	4,700
G.....	3-S	50-60	14.3					24	4,800	180	9,300
H.....	1-S	30	60	22	.7	.2	.6	12	3,300	180	5,000
I.....	4-S	40	52	32	3.0	1.2	3.0	20	4,360	155	
J.....	2-S	22	50	30	7.5	5.01	22.7	16	2,400	220	5,000
K.....	22-C	170	60	45	25	14.8	8.7	48	35,000	200	29,000

* K, Kalhperry towers; S, Skoglund towers; C, cascade type.

Typical operating costs for tower "J" for one year.

Power (200 watts per pipe, 300 days, at 2 cents per kw.-hour) ..	\$460
Labor, 2 hours per day at 50 cents per hour	\$300
Repairs (estimated)	\$200

With the exception of installations J and K, all precipitators were installed after the usual coke scrubbing towers and for the primary purpose of eliminating a nuisance. Installation J was made without coke scrubbers, but there was included in the system a cooling coil of 12-inch lead pipe, with return bends exposed to the air, having a total length of 125 feet.

When scrubbers are omitted the addition of such a cooling coil is advisable, because the precipitator efficiency is vastly improved when the gases are not hotter than 200 to 210° F. at the time of treatment.

The efficiencies of these installations have been consistently high. Continuous operation with clearances of 98 to 100 per cent have been

maintained. Where scrubbers have been omitted, tests have shown over-all concentrator efficiencies of 96 per cent, based on the amount of acid passed through the tower, the amount of concentrated acid produced, and the amount recovered in the precipitator reduced to the basis of 100 per cent sulphuric acid.

ACID-PROOF MASONRY.

In the preceding pages considerable mention has been given to the use of acid-proof masonry in the construction of Glover, Gay-Lussac, various types of intermediate towers, and various concentrating towers. Most acid-plant constructors are now prepared to erect such towers with acid-proof brick or tile, and the success of this construction for these towers seems assured. However, the construction requires careful design, the use of superior and proper grades of material, and the proper treatment or curing of the cement used. Certain types of cement have recently come onto the market under various trade names, such, for example, as "acid-proof cement," recommended and used by the Chemical Construction Co., and "duro" cement, used by the Process Engineering Co. In using these cements sodium silicate is used as a binder.

One of the chief objections to this type of construction has been the liability of the tower walls to crack and develop leaks when the towers are subjected to any considerable differences in temperature.

One of the most recent designs of towers, etc., for hot gases and acids is that controlled by the Kalbpery corporation.

Referring to figures 17 and 18, it may be noted that the construction comprises an inner inclosure for the liquids and gases, composed of several relatively movable wall sections so that expansion and contraction can take place with minimum of cracking of these walls; that the inner inclosure is surrounded with an outer inclosure consisting of a single wall; and that these two walls are separated by an air space closed at the top, open for the passage of liquids to the interior of the structure at the bottom, but sealed at the bottom against passage of gases, thus making the air space dead.

The inner walls are supported by means of special brick which may be laid in either the outer or the inner wall; preferably in the outer, as the rounded projections then present only a line contact with the inner wall, and offer the least path for any liquid escaping through the inner wall to flow over to the outer wall.

It will be seen that this construction permits movement of the inner walls with comparative freedom from strain, as they are free to move in one direction, and that the tendency of the walls to crack is reduced to a minimum.

In the installation shown in the illustrations the inner and outer walls are joined by completing the masonry into a common wall, though this construction need not necessarily be followed, and the space at the top may be closed by some other form of cover connect-

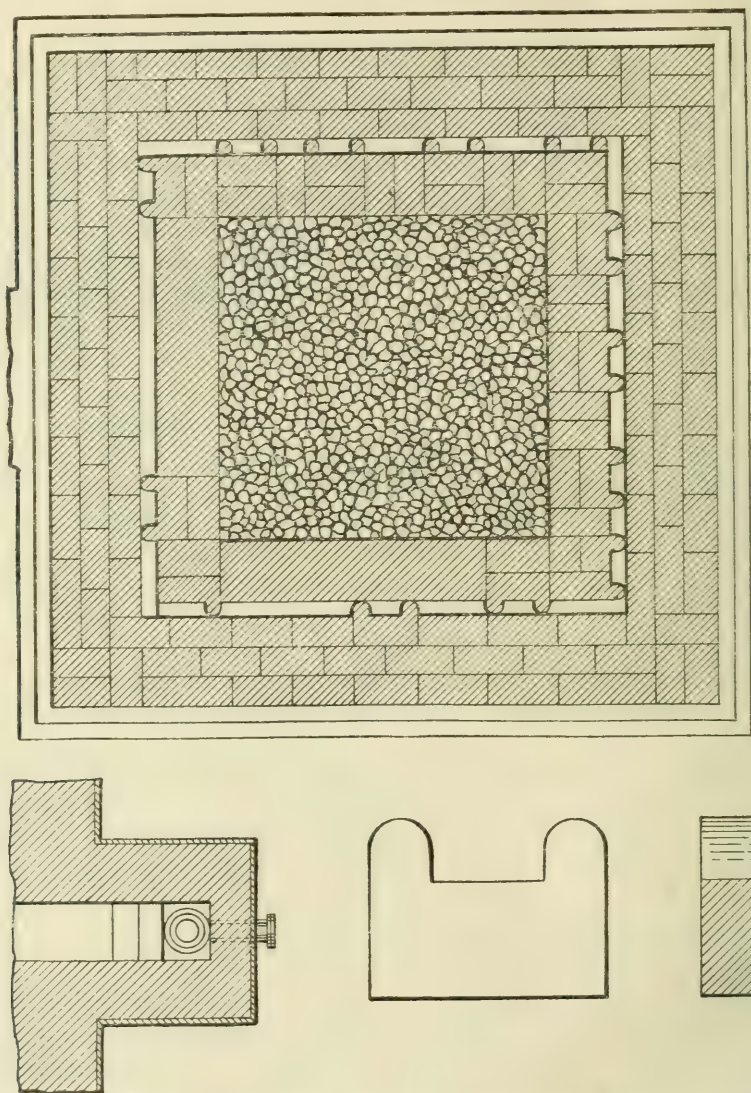


FIGURE 17.—Kalbpery, acid-proof masonry, cross section.

ing the two walls and yet providing for less rigid construction, if desirable. However, the rise of temperature at this point is very little above the normal; therefore the expansion is almost negligible.

It is true that a small amount of liquid passes out through the open joints at the junction of the inner walls, together with that

which finds its way through the inevitable cracks formed in the inner walls. The proportion of the total liquid content that comes

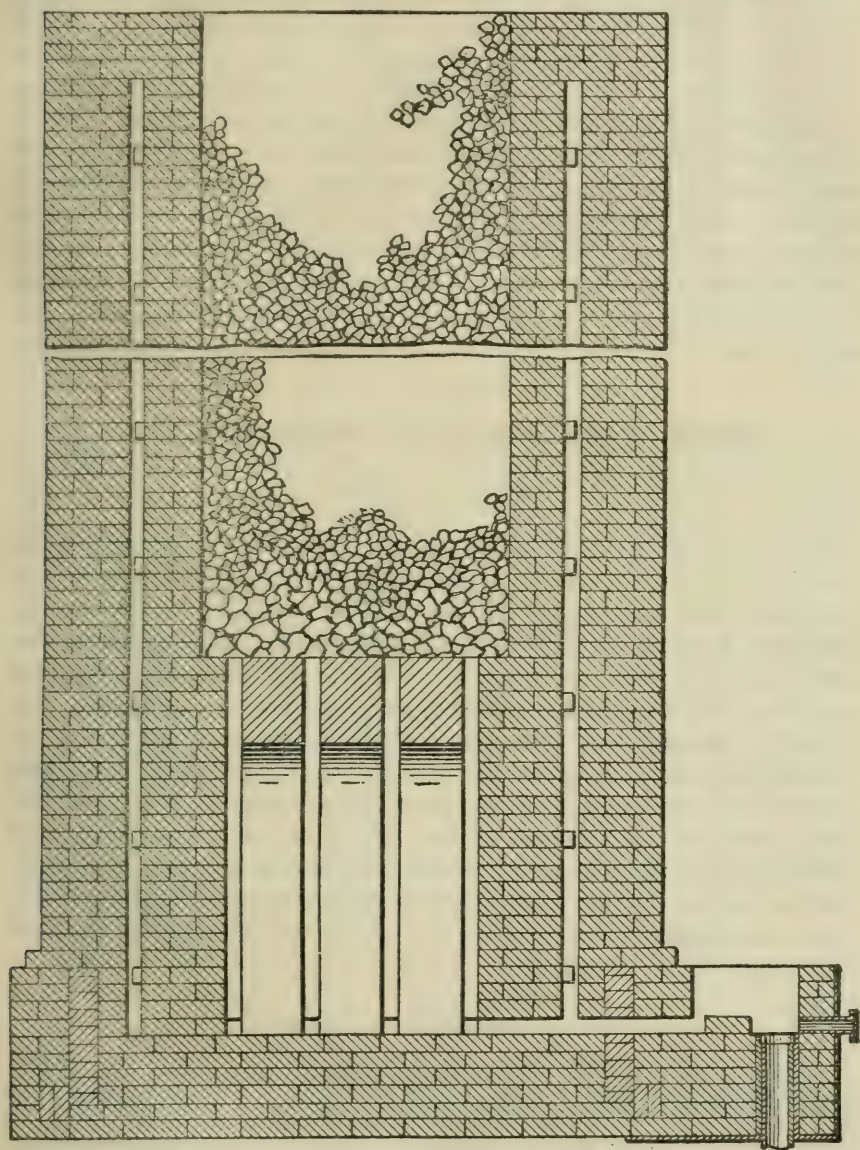


FIGURE 18.—Kalberry acid-proof masonry, elevation.

in contact with the interior surface of the inner wall is, however, very small, and of that proportion only a small percentage will find its way through into the space between the inner and outer walls, so

that the total amount reaching that space and flowing downward between the walls is negligible.

On account of the dead-air space between the walls, the outer walls are maintained at a comparatively low temperature, with the result that there is little or no expansion of the outer walls. The base is inclosed in a metallic pan in order to guard against the escape of liquid through any cracks which might form in the base.

One advantage of this construction is that it is built throughout with standard brick, requiring a minimum amount of sheet lead, with no steel other than the four corner angles and the tie-rods. The corner angles are extended to carry the feed tank and feeding apparatus, which is not shown. The only part that is not standard stock material is the special brick having a semicircular lug formed on the side. These are not difficult to make, requiring only a simple die.

ACTION OF SULPHURIC ACID ON LEAD OR IRON.

ACTION ON LEAD.

Up to a strength of about 60° B. the action of sulphuric acid on lead is very slight, even when heated to near the boiling point. If the acid is boiled, however, the lead is strongly attacked. At strengths ranging from 60° B. (77.67 per cent H_2SO_4) to 96 per cent H_2SO_4 , the action is still only slight in the cold. However, the action increases as the temperature rises, the lead being rapidly dissolved by the ordinary concentrated sulphuric acid at about 250° C. Monohydrate acid acts quite strongly and fuming acids energetically attack the lead even at ordinary atmospheric temperatures. At ordinary temperatures and even up to 100° C. the purest lead is least attacked by the sulphuric acid. Impurities, such as bismuth, antimony, zinc, or copper, have a deleterious effect, but for very high temperatures the addition of a little copper (0.1 to 0.2 per cent) to the lead appears to be of advantage.

ACTION ON ORDINARY CAST IRON.

Acids of all strengths from chamber acid to 100 per cent H_2SO_4 have very little action on cast iron at ordinary temperatures. If boiling, the weaker acids attack cast iron vigorously. The action decreases as the strength of the acid increases, until at 98 per cent H_2SO_4 the iron is scarcely attacked at all. Fuming acids below 20 per cent SO_3 have a somewhat greater action than 98 to 100 per cent H_2SO_4 , but above that strength the action practically ceases.

Cast-iron vessels, however, are not suitable for the manufacture of fuming acids, owing to the fact that the free SO_3 penetrates into

the pores of the metal, producing strains (probably due to the formation of gases in the pores by action of the acid and carbon) which causes the metal to break suddenly without any warning.

ACTION ON WROUGHT IRON.

Acids below 100 per cent H_2SO_4 act more rapidly on wrought iron than on cast iron, especially at high temperatures. However, in the cold the action is very slight with acids above 60° B. (about 78 per cent H_2SO_4). Wrought iron is somewhat attacked by fuming acids at a concentration of about 10 per cent free SO_3 , but the action decreases as the strength of the acid increases and at 27 per cent free SO_3 it is negligible.

ACTION ON ALLOYS OF IRON AND SILICON.

Alloys of iron and silicon (tantiron, corrosiron, duriron) are much less attacked by boiling acids than is ordinary cast iron, and may be used in concentrating weak acids up to 98 per cent H_2SO_4 . Fuming acids, however, energetically attack these alloys.

STORAGE TANKS.

It is desirable to have at the head of each Glover tower or Gay-Lussac tower at least several hours' supply of acid. Tanks at the bottom of these towers should have at least a day's capacity, and the tanks for chamber acid may be of any capacity necessary for the economical operation of the plant. Plants producing acid for the custom market usually have ample storage to allow for the fluctuation in sales or for delays in delivery of cars, etc.

The low-strength acid storage tanks are generally of wood, lined with lead weighing 6, 8, or 10 pounds per square foot. Acid-proof chemical brick or tile may also be used for lining the tanks.

Closed storage tanks for 60° B. acid are made of steel or wrought iron, these materials being suitable where no air can enter, the moisture of which might dilute the acid.

Acid of 66° B. strength or higher is generally stored in riveted steel tanks, emptied either through a foot valve in the bottom surrounded by a low upstand to prevent the drawing of mud, or the tank has draw-off valves at various levels on the sides. These tanks are usually placed on structural steel or on concrete supports high enough so that the acid will run out into cars by gravity. A blow-off pipe about 2 inches in diameter should be provided near the center of the tank and extending fairly well down away from the manhole plate, so that the blast of air which follows the blowing of an "egg" into the tank may find free access to the outside atmosphere.

Storage tanks, especially for low-strength acid, may be made of reinforced concrete, the inner surface of which is painted with pitch and lined with lead.

In the foot-valve arrangement, a porcelain plug and seat is commonly used. The seat is arranged in place and supported by a wooden block, then molten sulphur is poured in around the seat to close the spaces between it and the concrete. The plug valves are operated either by screw stem or by lever. Asbestos-seated iron plugs or corks are frequently used where frequent opening and closing is necessary.

Sulphuric acid is shipped in tank cars, tank wagons, drums, and carboys. Tank cars have capacities of 60,000 to 160,000 pounds. They are usually provided with a small pump or well into which a "blow-off" pipe dips to empty the tank as completely as possible. Sometimes a foot valve or cork is provided on the bottom of the tank for emptying, but the better practice is to blow the acid out of the tank with compressed air. The tanks are usually provided with a dome having a manhole plate, the blow-off pipe being at one side of the manhole and the pressure air pipe at the other side, both being provided with a flanked flanged union, with a cork and a cap to protect the threads.

Drums are of various sizes, holding between 500 and 1,500 pounds of acid. Carboys are glass bottles of 10 to 12 gallon capacity, protected from breakage by a casing of some sort, and hold about 180 pounds of 66° B. acid.

CONTACT PROCESS FOR MANUFACTURE OF SULPHURIC ACID.

GENERAL DISCUSSION OF THE PROCESS.

Although the reaction between sulphur dioxide and oxygen is almost imperceptibly slow, even at 400° C., in the absence of a catalyst, yet by the presence of certain catalysts the reaction is brought about quite rapidly. A catalyst does not initiate a reaction or change the final equilibrium existing between the reacting substances: it merely affects the velocity with which the reaction occurs.

The contact process for the manufacture of sulphuric acid is based upon the fact that if pure gaseous sulphur dioxide and the proper proportion of oxygen are heated together in intimate contact with finely divided platinum, ferric oxide, or other catalytic material, a more or less complete and rapid oxidation of SO_2 to SO_3 will take place, providing the temperature of the reaction during the contact is not allowed to rise to the point of dissociation of SO_3 —that is, to the point where SO_3 will break up into SO_2 and O. The SO_3 vapor formed by the reaction can then be recovered by cooling and by absorption in a solution of strong acid.

The various contact materials, besides metallic platinum, which have been tried as catalysts include oxides of iron, chromium, tin, bismuth, tungsten, titanium, molybdenum, thorium, and vanadium.

With the exception of ferric oxide, which has been used for one application of the contact process known as the "Mannheim" process, none of these has been successfully used. Ferric oxide, moreover, has not been as successfully used as has platinum, for the following reasons:

From numerous carefully observed and recorded experiments it has been determined that the temperatures which, under normal pressures, yield the highest conversion to SO_3 with any practicable mixture of SO_2 and air, range from 425° to 450° C. Above these temperatures the SO_3 does not completely form or that which is formed begins to decompose again into SO_2 and O_2 . Platinum at these temperatures has the desired catalytic effect—that is, it increases sufficiently the velocity of the reaction, $\text{SO}_2 + 0.5\text{O}_2 = \text{SO}_3$, to produce within a reasonable time almost quantitative conversion to SO_3 . On the other hand, iron oxide at these temperatures does not exhibit the same sufficient catalytic action by way of increasing the velocity of the reaction as does platinum, and its use is not practicable at these temperatures. Only at 600° C. does the iron oxide become sufficiently active as a catalyst to permit its use. However, at such temperatures the reaction is not complete or the SO_3 is largely broken down into SO_2 and O_2 again. In fact, the maximum yield obtainable, both from theoretic considerations and observed phenomena, is only about 70 per cent SO_3 . In practice the yield is more nearly 40 to 50 per cent.

Thus, platinum is the most effective contact substance now in use, and the contact-acid industry of the country is based on the use of that material in one form or another.

A mixture of sulphur dioxide and oxygen reacts energetically when first brought into contact with the heated platinum, but the reaction takes place more and more slowly as an increasing percentage of SO_3 is formed, and the final conversion of SO_2 into SO_3 is only attained by allowing the reacting gases to remain in contact with each other in the presence of the platinum for some considerable time. The higher the temperature the more rapidly is the final conversion attained, but as the back action ($\text{SO}_3 = \text{SO}_2 + \text{O}$) increases rapidly at the higher temperatures, the less favorable is the final result at these temperatures. This is shown clearly in figure 19, giving the equilibrium maximum values for the conversion of SO_2 to SO_3 obtained by Bodenstein and Pohl, as stated by Martin.^a

^a Martin, Geoffrey, *Industrial and manufacturing chemistry*, Part II, *Inorganic, Sulphuric acid* (conditions for technical success, pp. 241–242), vol. 1, 1917, pp. 207–256.

TYPES OF PLANTS IN USE.

There are four general types of contact-process acid installations in use in this country, known, respectively, as the Mannheim, Badische, Grillo-Schroeder, and Tentelaw. In all of these processes many of the individual steps in the manufacture are similar, and frequently the same apparatus is utilized. The mechanical application of the principle involved varies according to the individual ideas of the designer, so that, as a whole, the processes are more or less similar or interchangeable. This applies especially to the last

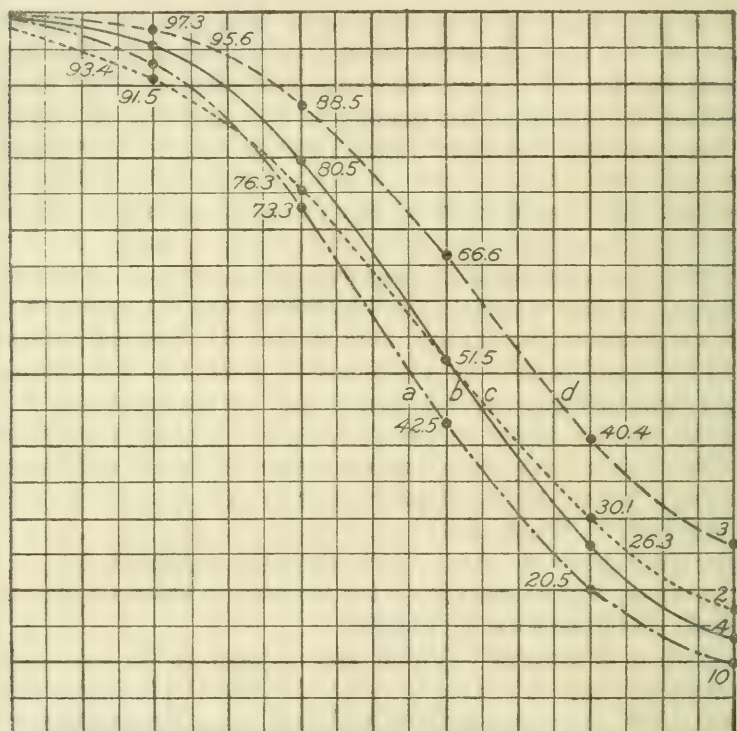


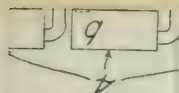
FIGURE 19.—Diagram for conversion of SO_2 to SO_3 (after Bodenstein and Pohl).

three processes mentioned, all of which employ platinum as the sole material for obtaining oxidation.

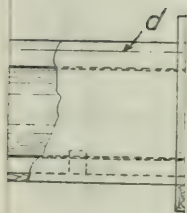
The Badische and Tentelaw systems differ from the Grillo-Schroeder especially in utilizing asbestos instead of magnesium sulphate as the carrier for the platinum.

The Tentelaw system differs from the Grillo-Schroeder and the Badische especially in its heat-transferring and gas-preheating apparatus.

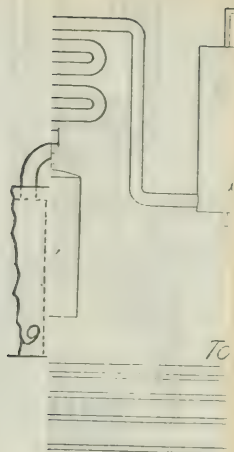
The Mannheim system differs essentially from the other three in that ferric oxide is used to obtain a part of the oxidation, and



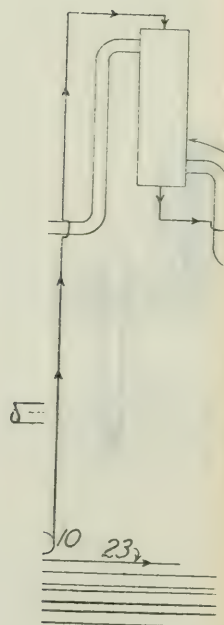
14, blow case; 15, su
O₂ gas (cold); 35, SO



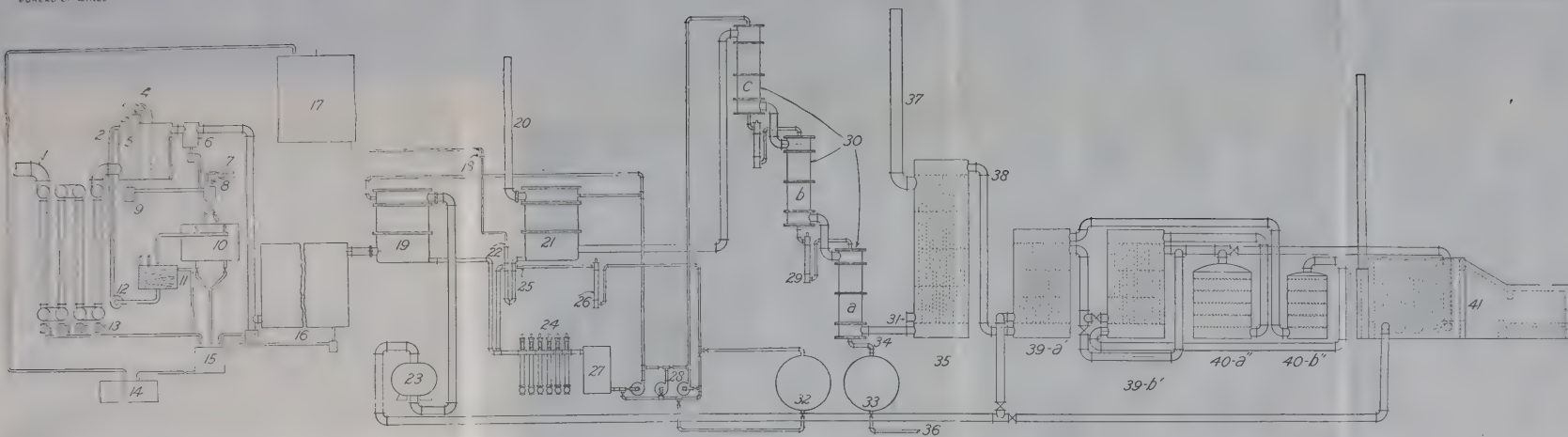
g, drain.



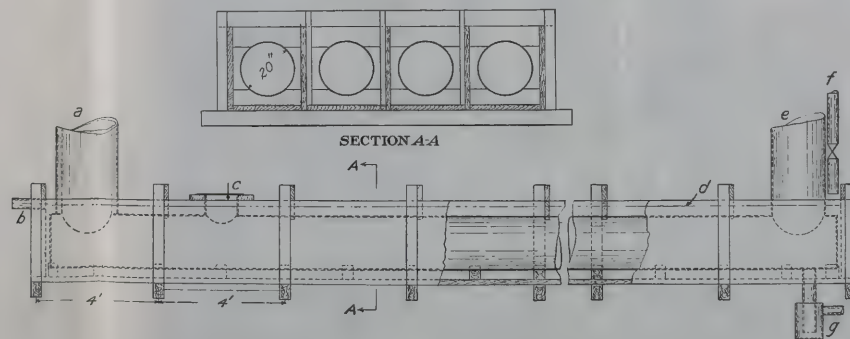
1, C
lower; 14, preheating
acid cooler; 24, overf



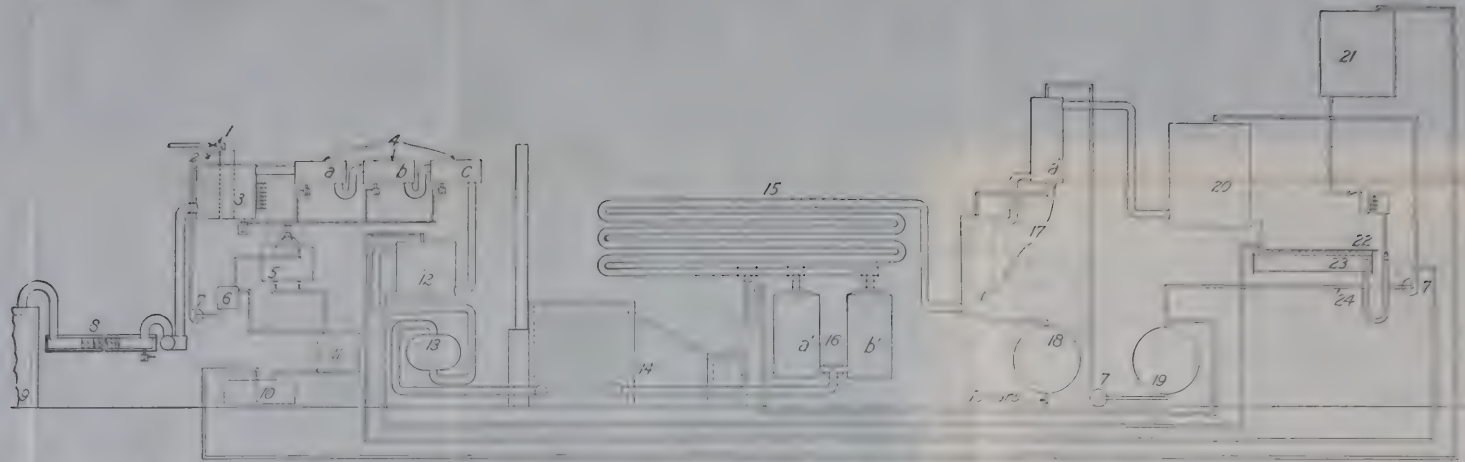
1, Weak
acid to storage; 15
a, b, platinum shaft



1, SO₂ inlet; 2, scrubber; 3, overflow; 4, cooling water inlet; 5, scrubber; 6, spray catcher; 7, fresh acid inlet; 8, water inlet; 9, acid outlet; 10, twin setting tanks; 11, coolers; 12, pumps; 13, gas coolers; 14, blow case; 15, sump; 16, coke filter; 17, weak acid; 18, sight feed; 19, drier; 20, waste gas stack; 21, absorber; 22, weak acid; 23, inlet; 24, air inlet; 25, cooling water inlet; 26, overflow; 27, tank; 28, pump; 29, acid cooler; 30, a, b, c, oleum towers; 31, air inlet; 32, tank for 99 per cent acid; 33, tank for oleum; 34, SO₂ gas (cold); 35, SO₂ gas cooler; 36, to loading station; 37, stock; 38, SO₂ gas (hot); 39, a, b, heat exchanger; 40, a, b, heat exchanger; 41, preheating furnace used in starting.

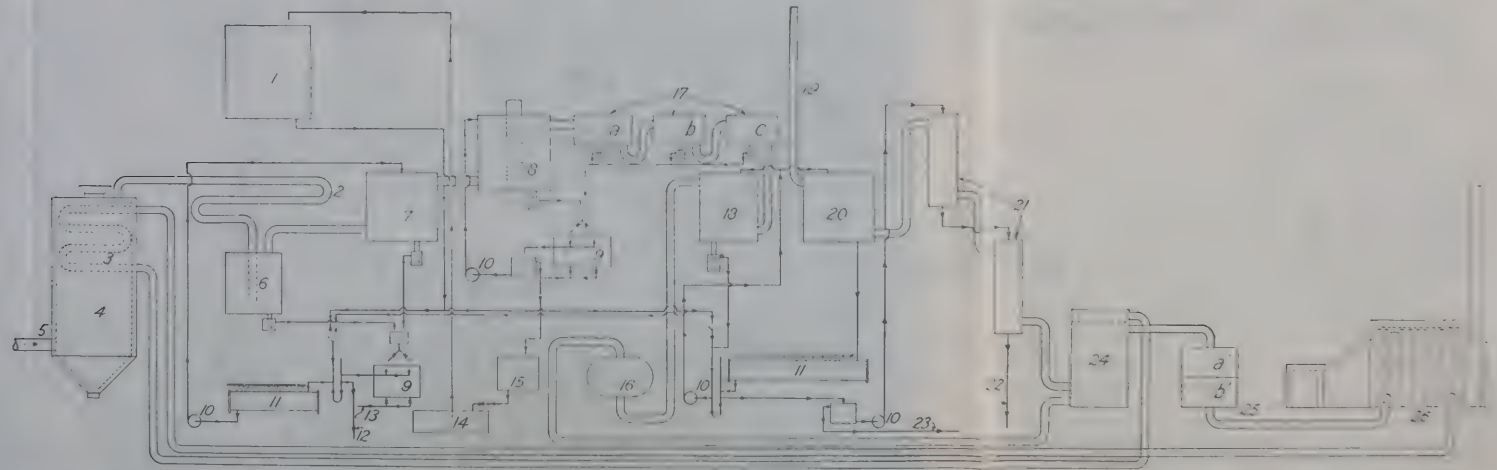


a, Gas inlet; b, water inlet; c, washout; d, water level; e, gas outlet; f, cooling water; g, drain.



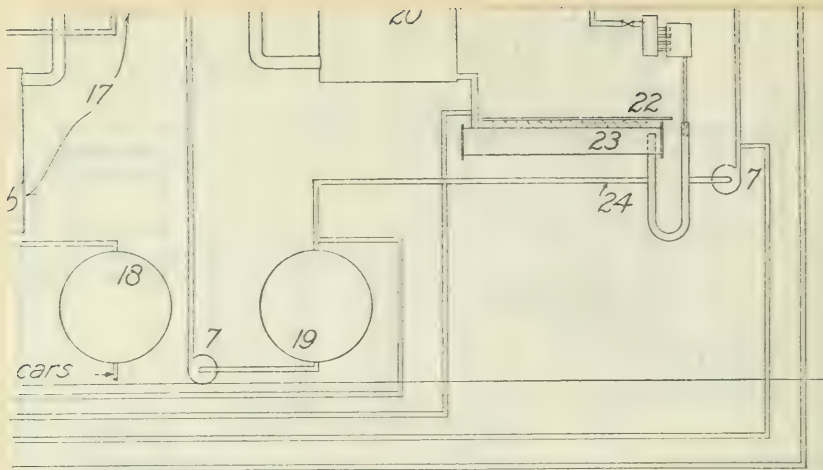
A. GRILLO-SCHROEDER SYSTEM, FLOW CHART.

1, 2, 3, 4, 5, 6, 7, 8, 9, 10, 11, 12, 13, 14, 15, 16, 17, 18, 19, 20, 21, 22, 23, 24. 1, Wear acid tank; 2, gas cooler; 3, heat transfer; 4, oxide shaft; 5, 50% inlet; 6, 50% outlet; 7, gas loader; 8, 50% inlet; 9, 50% outlet; 10, pump; 11, 50% inlet; 12, 50% outlet; 13, 50% inlet; 14, 50% outlet; 15, 50% inlet; 16, 50% outlet; 17, 50% inlet; 18, 50% outlet; 19, 50% inlet; 20, 50% outlet; 21, 50% inlet; 22, 50% outlet; 23, 50% inlet; 24, 50% outlet.

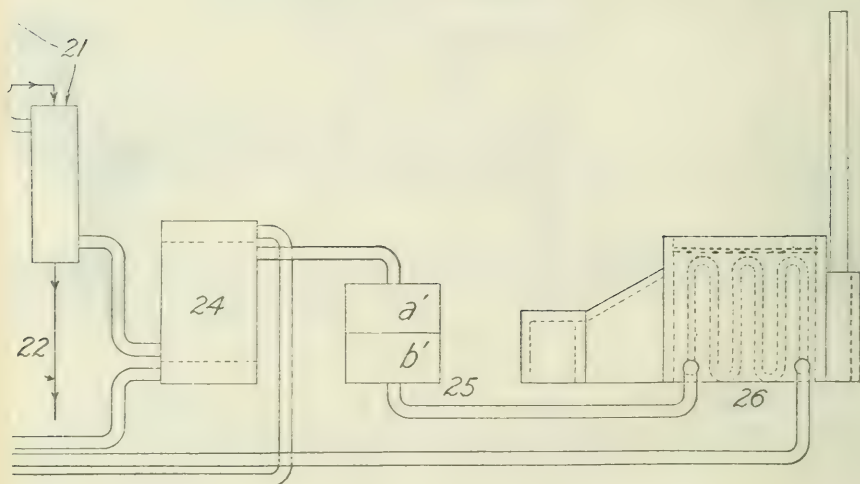


B. MANHIEM SYSTEM, FLOW CHART.

1, Wear acid tank; 2, gas cooler; 3, heat transfer; 4, oxide shaft; 5, 50% inlet; 6, 50% outlet; 7, gas loader; 8, 50% inlet; 9, 50% outlet; 10, pump; 11, 50% inlet; 12, 50% outlet; 13, 50% inlet; 14, 50% outlet; 15, 50% inlet; 16, 50% outlet; 17, 50% inlet; 18, 50% outlet; 19, 50% inlet; 20, 50% outlet; 21, 50% inlet; 22, 50% outlet; 23, 50% inlet; 24, 50% outlet.



furnace; 15, SO_3 cooling pipes; 16, a, b, converters; 17, a, b, oleum towers; 18, oleum storage; low.



. to sewer; 14, blow case; 15, sump; 16, blower; 17, a, b, c, filters; 18, drier; 19, waste gas stack; 26, preheating furnace.

this method necessitates a double absorption system and material changes in the design.

Briefly, the four types of plants include the following units:

Badische system (see Pl. XIV, A):

Pyrite ore roasters or sulphur burners.

Dust-catching installation.

Vertical lead-pipe cooling installation.

Gas-scrubbing installation.

Coke filter.

Gas-drying tower.

Blower.

Converters.

Vertical tubular heat transfers.

SO₃ gas-cooling system.

Absorption towers.

Oleum towers.

Grillo-Schroeder system (see Pl. XV, A):

Pyrite ore roasters or sulphur burners.

Dust-catching installation.

Vertical or horizontal lead-pipe cooling installation.

Lead-coil gas cooling and scrubbing towers.

Asbestos, mineral wool, sawdust, or coke filtering system.

SO₂ gas-drying tower.

Blower.

Preheating furnace.

Converters, which may or may not be designed as heat transfers.

SO₃ gas-cooling system.

Absorption towers.

Oleum towers.

Tentelw system:

The Tentelw system is essentially the same as either the Badische or Grillo-Schroeder systems, or a combination of both, except that its heat transfer and preheating system differs radically from that used in either of the other processes, as has been previously described.

Mannheim system (see Pl. XV, B):

Lump-ore burners, to which a certain proportion of sulphur burners may be added, if desired.

A ferric oxide shaft, together with heat transfer or forewarming chambers.

Oxide shaft coolers and sludge settlers.

Oxide absorption towers.

Fan.

Acid catchers.

Gas filters.

Preheaters or heat transfers.

Superheaters.

Platinum shafts.

Final absorption towers.

Oleum towers.

The New Jersey Zinc Co. was the owner of the Grillo-Schroeder patents, the main features of which expired in 1918. It used them in connection with the manufacture of acid from its zinc ores, and also issued licenses to other companies in the United States.

The Badische, Tentelew, and Mannheim patents are owned or controlled by the General Chemical Co. At one time objection was raised by the General Chemical Co. as to the right of the New Jersey Zinc Co. to use and to license for others the use of the Grillo-Schroeder process, and suit was commenced. However, an agreement was reached which, while allowing the New Jersey Zinc Co. and its licensees to continue to operate, gave the precedence for future licensing to the General Chemical Co. Although many of the features of these patents have expired, the General Chemical Co. claims still to control the process until 1923 and issues a license and requires the payment of royalties for the installation and operation of all contact plants, including those operating under the features of the Grillo-Schroeder patents.

ESSENTIAL CONDITIONS IN MANUFACTURE OF ACID BY CONTACT PROCESS.

The contact process, as practiced in this country for the manufacture of sulphuric acid, is based upon the two following essential facts:

1. When the sulphur dioxide (SO_2) gas, mixed with a suitable proportion of oxygen, is passed over heated platinum in a state of very fine subdivision, the reaction $2\text{SO}_2 + \text{O}_2 = 2\text{SO}_3$ takes place, forming sulphur trioxide or sulphuric acid anhydride (SO_3).

2. Sulphur trioxide is quantitatively absorbed by sulphuric acid solution of between 97.5 and 99.5 per cent H_2SO_4 content, resulting in the uniting of the SO_3 with the excess water in the sulphuric acid solution and the consequent formation of sulphuric acid (H_2SO_4).

Generally speaking, the range of sulphur dioxide strength in the gases treated in contact plants varies from 4 to $7\frac{1}{2}$ per cent SO_2 by volume. As a large excess of oxygen above the theoretical is necessary for complete oxidation of sulphur dioxide by the contact process, when burning pyrite it is not safe to have the SO_2 content of the gas higher than 7.5 per cent, otherwise the oxygen will be too low. When brimstone is burned as the source of sulphur dioxide, the gas will contain a higher proportion of oxygen in relation to its sulphur dioxide content than when burning pyrite; therefore, a gas

of higher sulphur dioxide content (up to $8\frac{1}{2}$ or even 9 per cent) may be utilized.

The gases, whether derived from the oxidation of pyrite or from the burning of sulphur, must be thoroughly cleaned from all solid impurities or fumes before entering the catalytic material in order to avoid the contamination of this material and consequent loss of efficiency. The gases must also be freed from certain gaseous impurities which have an inhibiting effect upon the oxidizing power of the catalyzer. A certain amount of sulphur trioxide (SO_3) will always be present in the gases, and this should be completely removed. The gases will be saturated with sulphuric acid in proportion to their vapor tension at the temperature at which they are being treated, and this sulphuric acid should be removed as far as possible by dehydrating the gases with strong sulphuric acid before they are permitted to enter the catalytic material. This latter precaution is not especially essential but is highly advisable in order to prevent the deposition of sulphuric acid throughout the system prior to entering the absorption towers, as the condensing of acid upon a steel or cast-iron system results in continuous and heavy deterioration of plant. Oxidation of the sulphur dioxide to sulphur trioxide with platinum catalyzer begins at a temperature of about 360°C. , but, as stated previously, in ordinary working practice it is customary to carry this temperature considerably higher, say about 420°C. If the platinum catalyzer is foul or "poisoned," its activity may be considerably increased by raising the temperature of the gases, and in some instances this has been done even to as high as 550°C. This procedure is not advisable, however, and the catalytic material should be removed and revived by proper treatment before its efficiency has become so impaired.

The oxidation of sulphur dioxide to sulphur trioxide is a very exothermic reaction, and as this reaction is also reversible at high temperatures care must be taken that in the so-called converter itself the temperature is not allowed to rise too high (preferably never above 550°C.) in order that the oxidation may be maintained at its highest efficiency.

The gases, containing sulphur trioxide, after leaving the converter, should be cooled before entering the absorption installation, preferably to a temperature of 50° or 60°C. or lower. The sulphuric acid used for absorption is heated both by the sensible heat of the gases passing through it and also by the heat of formation of the sulphuric acid formed by the uniting of the sulphur trioxide with the water in the acid solution. This acid must be continually cooled and preferably held down to a temperature of 40°C. or 50°C. , as sulphur tri-

oxide is not readily or completely absorbed in sulphuric acid solution when the temperature rises too high.

The strength of the absorbing acid must be very carefully maintained and should never vary more than 1 per cent either way from a content of 98.5 per cent H_2SO_4 .

If oleum (fuming sulphuric acid) is to be manufactured, this is accomplished by passing the cool gases containing SO_3 through strong sulphuric acid until the acid, through absorption and solution of SO_3 , has reached the desired strength. This solution of sulphur trioxide in sulphuric acid to produce oleum also generates heat, and suitable cooling apparatus must be installed and operated in order to attain oleum of desired strength.

COOLING THE SO_2 GASES.

The precipitation of the heavier dust and fume is fully discussed elsewhere in this bulletin under a separate heading, and will not be considered further at this point. The gases, containing a relatively small proportion of impurities, should be drawn from the dust and fume catching installation at a temperature in the neighborhood of 280°C . and then go into a lead cooling system. The first part of this lead cooling system generally consists of large and heavy-walled pipes, banded at frequent intervals on the outside with steel bands, which in turn are covered with thin sheet lead securely burned to the main lead pipe. This banding is necessary to prevent collapse of the large lead pipes, which are under a partial vacuum caused by the suction of the blower further along in the system. The lead pipes are water cooled and the sheet-lead covering of the bands is necessary not only to hold the lead pipes against the bands and maintain their form, but also to keep the cooling water away from the bands themselves, as, especially if impure or salt water be used for cooling, an electrolytic action is set up between the steel and the lead, and the steel band is rapidly eaten away and becomes useless. The lead pipes are usually 12 to 20 inches in internal diameter and a number of them are installed in parallel, the number and size depending upon the amount of gas to be handled, its temperature, and the individual ideas of the designer.

In some plants the lead pipes are installed horizontally, and in an installation of this type (see Pl. XIV, *B*, p. 150) to handle a large amount of gases, the pipes are usually made of large diameter and very long in order to obtain the cooling service required with a minimum installation cost. These pipes may be either submerged in water boxes or sprayed. There are several disadvantages connected with this form of installation, because a considerable amount of very fine flue dust, fume, together with sulphuric acid, is precipitated in the pipes. The sulphuric acid may be removed by means

of "boots" installed at frequent intervals along the bottom of the pipes, but enough does not condense to wash out the precipitated dust and fume. Consequently large cleaning holes have to be installed in the tops of the pipes, and the covers of these holes have to be removed and the pipes thoroughly flushed out with water at frequent intervals.

A more efficient and less troublesome type of installation is parallel sets of vertical banded lead pipes, usually about 12 inches in diameter, running from a common header above to a header below. Several such sets are constructed side by side with the headers of each set connected alternately at the top and bottom with the headers of the next set. The gases usually enter the top

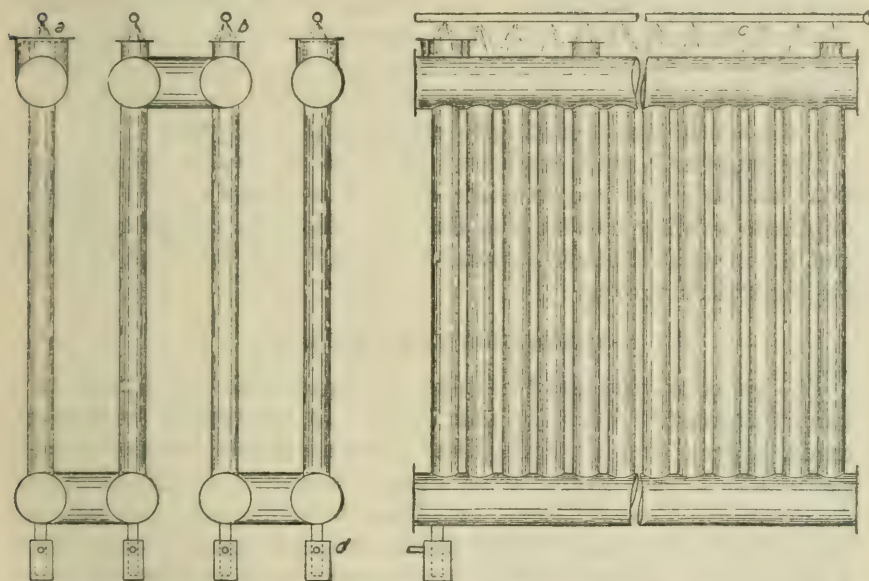


FIGURE 20.—Vertical lead cooler for SO_2 gases. *a*, SO_2 inlet; *b*, water spray; *c*, wash-out holes; *d*, drain.

header, pass down through the lead pipes in parallel into the lower header, pass from that header into the lower header of the next following set, thence up through the lead pipes of the second set into its top header and from there into the top header of the third set, etc. The vertical pipes are sprayed with water and the bottom headers of each set are provided with overflow "boots" of large size to permit draining off the condensed acid and also to permit opening one end and quickly and thoroughly flushing out the accumulation of dust or fume from time to time. The size of the vertical lead pipes is diminished in each succeeding set, as the gas volume diminishes due to the lowering of the gas temperature, but the number of pipes in each parallel set is usually the same. This

type of installation (fig. 20) is decidedly more expensive to erect than the horizontal type, but is much more efficient and less costly and troublesome in operation.

Great care must be taken in building the connection between the dust chamber and the lead system, as the temperature of the gases must be maintained at about 280° C. to avoid condensation of acid in the brick, concrete, or steel dust chamber. At times the gas temperature may rise considerably higher than this, bringing it to a point perilously close to the melting point of lead. An expensive but very good type of connection is lead-covered terra-cotta pipe, the terra cotta not being acted upon by any condensing acid or by the heat and serving to keep the heat to a large extent away from the lead covering. This type of connection may be installed as far as that point where the construction permits continuous water spraying of the lead, when all danger from overheating passes. Special care should be taken in the design of this part of the plant, in order to avoid continuous operating troubles and plant repairs.

The sulphuric acid condensed in these coolers is usually very weak and is either run to waste or more preferably run through a duplicate settling system, the dust and dirt allowed to settle out, and the clear acid above drawn off into a "blow case" and used in the absorption towers.

SCRUBBING THE SO_2 GASES.

The gases leaving the lead-pipe cooling system are usually at a temperature of between 40° and 70° C. In addition to sulphur dioxide, oxygen, and nitrogen, these gases are liable to contain some residual dust, lead or zinc fume, arsenic, selenium, or sulphuric-acid vapors, and chlorine, arsine, or silicon tetra fluoride, and possibly even other impurities. All of these impurities must be removed if a plant is to operate without interruptions and at high efficiency. Practically all of these impurities may be removed by an extremely thorough scrubbing with sulphuric-acid solution of fairly low strength. Many of the impurities, such as the dust, various fumes, and some of the deleterious gases, may be removed by scrubbing with nearly any strength of acid, but chlorine, which is one of the most common and subtle contact poisons, is not wholly removed by scrubbing with strong acid, hence it is advisable to scrub with an acid of less than 30° B. Scrubbing with such a weak acid has the disadvantage, however, of leaving in the gases a considerable amount of water vapor, which later on is precipitated as sulphuric acid and causes serious trouble. For this reason, especially, it is advisable to constantly test the scrubbed gases for chlorine content and to scrub with as strong an acid solution as practicable, at the same time removing all of the chlorine.

Many methods of scrubbing have been tried, such as spray towers, vapor towers, perforated plate towers, lead-coil cooling and scrubbing towers, and bubblers or washing towers, but of all these various types only the last two have proved completely satisfactory and effective.

LEAD-COIL COOLING AND SCRUBBING TOWER.

There are several modifications of the lead-coil cooling and scrubbing system, all fairly effective. One of the best designs (see fig. 21) comprises an annular space between an outer and inner vertical lead shell, this space being filled with spirals of lead pipe with very little clearance between the pipes—not more than one-fourth to three-eighths inch. Each spiral is staggered in relation to the spiral just under it, so that the center of the pipes in one spiral is always just over the center of the orifice between the pipes in the spiral below. Fifteen to 30 of these spirals, as necessity may demand, are superimposed one over the other in the space between the outer and inner lead shell mentioned. One end of each spiral is burned into the wall of the inner shell, which serves for a reservoir for water supply. The

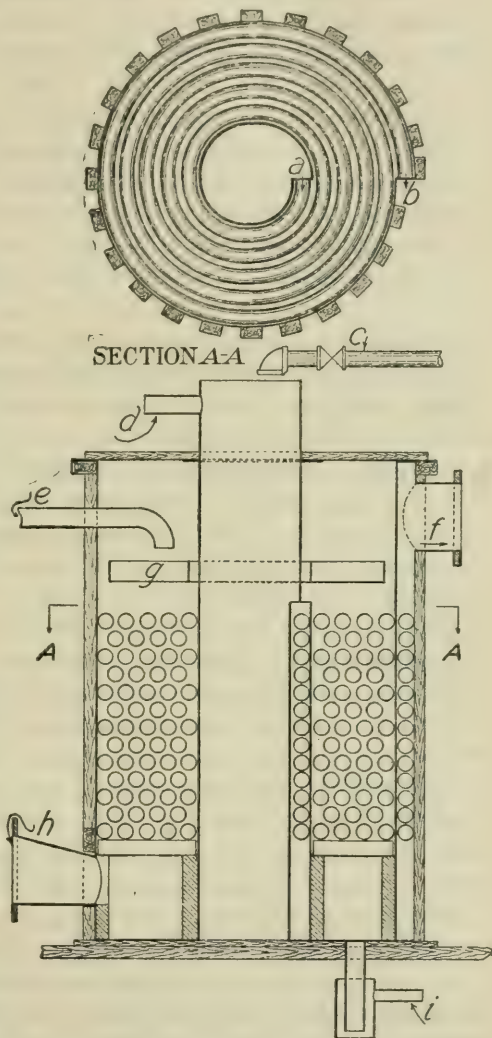


FIGURE 21.—Lead-coil cooling and scrubbing system; *a*, water inlet; *b*, water outlet; *c*, cooling water; *d*, water overflow; *e*, acid inlet; *f*, gas outlet; *g*, pan; *h*, gas inlet; *i*, acid outlet.

other end of the spiral protrudes through and is burned into the wall of the outer shell. The inner shell is kept filled with water; the flow of water through each spiral is regulated by means of a valve attached to the end that protrudes through the outer shell. The hot, dirty gases enter the base of this tower and pass upward

between and around the water-cooled spirals. In this manner the cooling water does not come into actual contact with the gas and impart moisture to it. Weak sulphuric acid enters the top of the tower and by means of a distributing pan is showered down over the water-cooled coils and against the upcoming hot, dirty gases. This scrubbing acid serves two functions. It removes all dirt, fume, and deleterious gases from the sulphur dioxide gases and leaves in the gases only moisture, in proportion to the vapor tension of the strength of sulphuric acid used at the scrubbing temperature. It also acts essentially as a cooler. The heat of the gases is not transferred through metal into water, which would only result in a transfer rate of approximately 2 to 3 B. t. u. per square foot of cooling surface per degree Fahrenheit difference in gas and cooling water temperatures in one hour's time, but goes directly into the scrubbing acid, which, in turn, can at no point drop more than one-half or three-eighths of an inch before coming into contact with another water-cooled lead surface. As a result the rate of heat transfer is greatly increased, ranging in actual practice from 20 to 80 B. t. u. per square foot per degree Fahrenheit difference per hour, or from 100 to 400 kg.-calories per square meter per degree centigrade difference per hour. The rate varies considerably with the speed of the gases and the fineness of division of the scrubbing acid in its downward passage through the coils.

The acid is discharged from the bottom of the tower through a trap into one of a duplicate pair of lead-lined settling tanks. The dirt, fume, and other solid impurities settle out and practically clean acid overflows from the further end of the settling tank, and is returned to the top of the scrubbing tower by means of a pump or air lift and reused for scrubbing. When the tank of acid has become too foul or saturated with chlorine, the alternate tank filled with fresh acid is cut in, and the tank of dirty acid allowed to settle. After settling, the clean acid above is drawn off and blown to the absorbing towers, the sediment is washed out into the sewer, and the tank filled with fresh acid. The strength of the scrubbing acid, as before stated, must be carefully regulated, which is done by the addition of water, and care must be taken that this water is very low in chlorine. The great advantage of this type of tower is effective cooling of the gases without cooling water coming into contact with the gases, so that the amount of moisture carried forward by the gases into the drier is comparatively small.

"BUBBLERS" OR WASHING TOWER.

In the "bubbling" or "washing" system of gas scrubbing, also, methods of application differ according to the individual ideas of the designer. One method comprises introducing the gas into the

base of a lead-lined tank or tower filled with water or weak sulphuric acid, where the gas stream is broken by means of a perforated plate extending across the tower above the gas inlet, or other suitable contrivance, into small streams or bubbles that rise through the scrubbing liquor and are cleaned thereby. This method is efficient but requires a large expenditure of power to overcome the head of the liquid in the tower.

Another method involves filling the tower with a suitable distributing filling such as is used in a Glover tower, and continuously circulating the scrubbing liquor countercurrent to the rising stream of gases by means of a pump. In either method clean water or weak acid must be continually added to the liquor and part of the liquor allowed to overflow, or else the whole charge of liquor must be changed as soon as it becomes foul.

The great disadvantage of this system is that there is no internal cooling of the scrubbing liquor during the scrubbing. It is practically impossible on a large commercial scale to cool the gases in the large lead-pipe coolers to lower than 30° C., consequently the scrubbing liquor itself soon becomes heated and the gases leave the liquor at the same temperature at which they enter. This results in the gases absorbing a large proportion of moisture from the weak, warm scrubbing liquor and is equivalent to adding that much steam to the gases. The temperature of the gases being still above atmospheric, they will continue to be cooled in the filtering and spray-catching system; a large amount of very weak acid will be precipitated out and a great deal of moisture will also be carried over into the drying tower. The net result is that more water is introduced into the gases than is allowable if the total output of the plant is desired to be in the form of fuming sulphuric acid (oleum). This excess moisture will occur as weak acid drips from the lead-pipe coolers and from the filtering and spray-catching system, as weak acid overflow from the scrubbing tower, and as moisture which must be removed in the drying towers. If the total amount of water which comes out of the system in the form of weak acid is too large to be completely utilized in the absorbing towers, and produce the high-strength acid desired, the excess over the amount actually needed must be thrown away, resulting, of course, in the loss of its sulphuric acid content. In some plants this excess of weak acid solution is concentrated by heaters and then used, but this plan is not desirable unless absolutely necessary.

FILTERING THE GASES.

The gases, after leaving the scrubbing system, carry more or less acid spray or mist, and also occasionally some impurities which have not been completely scrubbed out, such as traces of selenium, lead,

zinc, and arsenic. In order to insure that any or all of those foreign materials, if present, are removed the gas is filtered. This filtering is performed in several different ways and with several different types of installation.

COKE FILTER.

One type of apparatus which has proved very successful and is used quite extensively is the coke filter (fig. 22). This is nothing more than a very large rectangular lead-lined box filled with carefully sized and washed coke. For filtering a sufficient volume of gases to produce 30 tons of sulphuric acid daily, this box would be about 30 to 40 feet wide, about 50 to 60 feet long, and about 12 to 15 feet deep. The sides, ends, top, and bottom are lead lined throughout. The bottom is not flat, but slopes slightly toward the center from both sides, and a shallow drain or trough runs longitudinally through the center of the bottom for its full length and discharges at one end through a boot or trap. This central drain and discharge serves to carry off the precipitated weak acid, together with whatever dirt or mechanical impurities is washed down with the acid. The gas entrance is situated centrally in one end and near the bottom; the discharge is in the other end and usually near the top. A large gas-diffusing space is usually constructed around the gas inlet and outlet on the inside of the filter box. This may be so constructed as to give a large area for uniform diffusion of the gases into the coke and still not become plugged with the fine coke. A grill is also built over the discharge trough in the center of the bottom. The whole box is filled completely with carefully sized and washed coke. One-quarter-inch to three-eighths-inch lumps are used, all fines being carefully washed out. After the coke is all in and well settled into place, the lead top is put on and burned onto the sides. Lead strips or lead-covered ribs extending across the filter box on the under side of the top and projecting well down into the coke should be installed at frequent intervals, so that if there is any further settling of the coke after the top is burned in place the gas will not have an uninterrupted flow through the open space left between the coke and lead cover.

The gas enters at one end of the filter box, diffuses into the coke, and traverses the coke-filled box longitudinally, finally going out at the other end.

The coke catches all the spray and mist, also whatever fume has not been scrubbed out, and these trickle down and are discharged from the drain in the bottom of the filter box.

This type of filter is expensive to install, but is self-draining and operates satisfactorily, providing the gases are scrubbed very free from solids, especially lead and arsenic. If this is not done, washout holes may be made in the top of the filter box, and the soluble

solids and some of the insoluble solids partly washed out from time to time. However, such operation is not very successful, owing to channeling of the water, and if any large accumulation of solids,

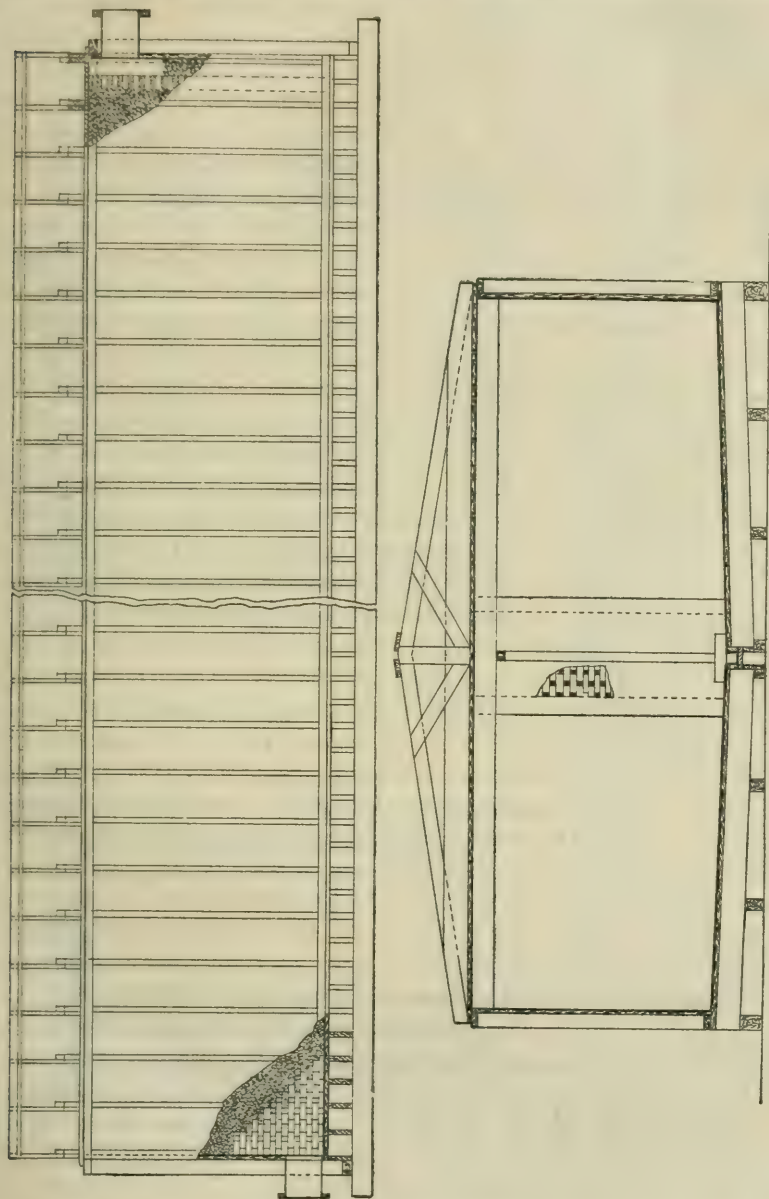


FIGURE 22.—Coke filter for purifying gases from scrubber.

especially lead fume, gets by the scrubbing system the coke filter will eventually plug, which necessitates taking the top off and renewing the coke. This is expensive and also necessitates a plant

shutdown of considerable duration unless a duplicate filter is installed, which is a heavy addition to the installation cost.

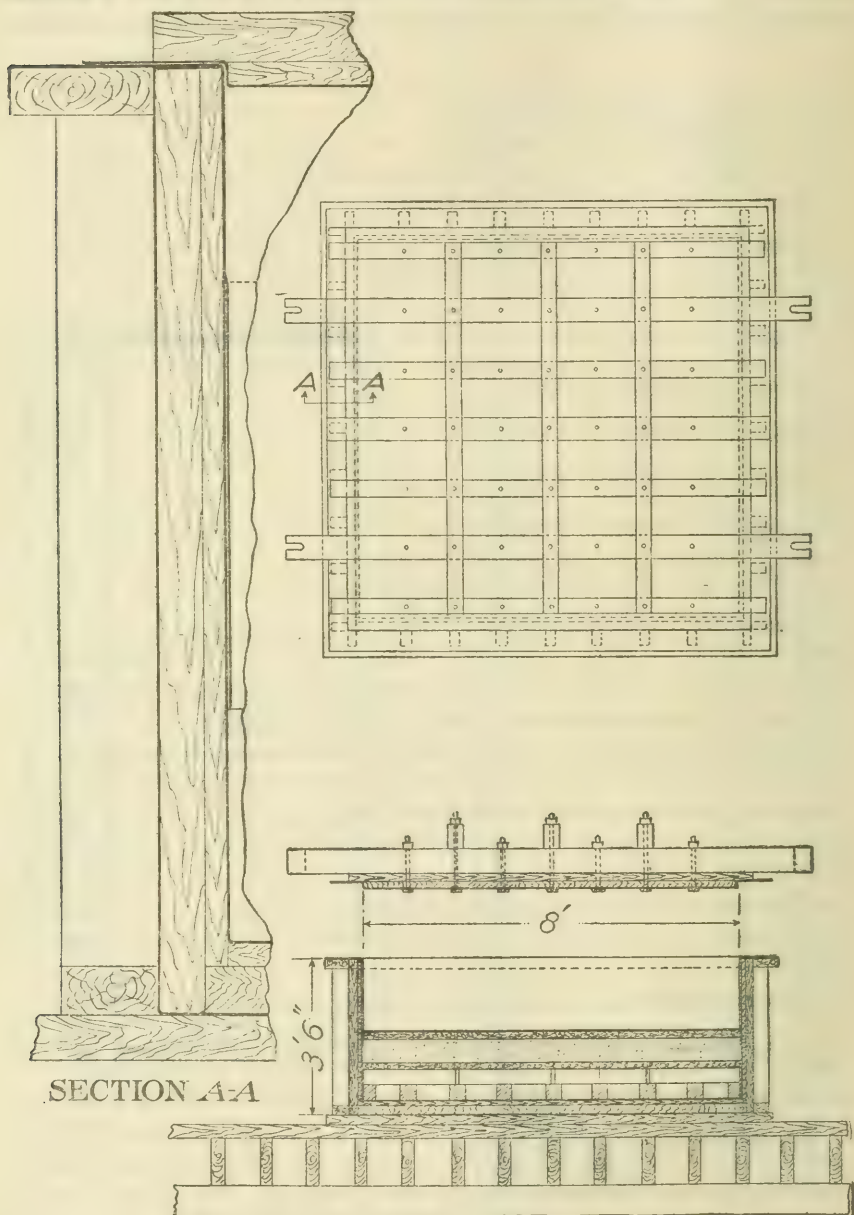


FIGURE 23.—Cross section of filter.

LEAD-LINED FILTER BOXES.

Another system of gas filtration which has proved very successful comprises a large number of small, lead-lined filter boxes gen-

erally arranged in sets of three in series, and as many sets as the quantity of gas to be filtered demands. (See fig. 23.) In addition, one or two extra sets are usually installed as spares to cut in to replace sets which have become foul.

Each filter box is usually 8 to 10 feet square and $2\frac{1}{2}$ to 3 feet deep. The boxes are of substantial construction and are lead-covered inside and out. The boxes are under suction and the outer lead covering, which is backed up by the wooden box, has to withstand the suction pull. This is important, as these filters are not filled with a solid filling like coke which will hold the inner lead lining in place, and it is very difficult to hold light sheet lead from collapsing under suction unless backed solidly over its entire surface. At the top of the sides the lead is flared over so as to present a horizontal plane surface about 6 inches wide completely around the filter box.

The top is in one piece, lead-lined, and very heavily ribbed on the outside. Heavy timbers project out on the four corners, the projections being used as faces for raising the top by means of four hydraulic jacks. The lead lining of the top projects out about halfway on the horizontal lead flare of the sides. In order to render the box gas tight under suction it is only necessary to lower the cover into place, batten down the projecting edges of the lead cover against the lead below, and lute the junction with a plastic material such as a mixture of Portland cement and soft cup grease. The gas entrance is in the center of one side and near the top; the gas exit is in the center of the other side and near the bottom.

As previously stated, these filter boxes are usually arranged in straight-line sets of three in series. Each box contains an acid-proof brick or tile grill covering the bottom and occupying about 1 foot of the depth of the box. On top of this grill is spread a layer of straw. On top of the straw in the first box of the series is placed about 6 inches of fairly coarse pine sawdust, which is covered with coarse burlap to prevent its being blown away at the point of gas entrance immediately above it.

The second filter box also contains about 6 inches of sawdust, covered with a thin, hand-packed layer of finely fluffed, long-fiber asbestos, with burlap on top of the asbestos.

The third filter box is sometimes filled the same as the second box, but frequently the asbestos and part of the sawdust is replaced with a layer of mineral wool, which has the property of absorbing chlorine and acts as a safety factor in case any chlorine gets by the scrubbing system. These filters all operate with a downward gas flow and are very efficient when operated in this manner. Experiment has demonstrated that they are not effective when the direction of gas flow is reversed.

Each individual filter box is provided with a tapped drain through which the acid, if any is caught, drips into a catch tank or blow case. Under normal operation there is a very considerable and constant drip from the first filter box and occasionally there is a small drip from the second box, but there should never be any drip from the third and last filter.

On each filter box is a differential pressure gage to show the resistance to gas passage through the filtering medium, and continuous readings are made and recorded. The record shows quickly when a filter is becoming plugged; then the whole set is cut out and a fresh set cut in with no plant shutdown. The filling in the set which has been cut out is then removed and replaced with fresh material. Ordinarily the first filter has to be renewed every seven or eight days, the second filter every three or four weeks, and the final filter every six or eight months.

In a set of three filters built as above described each square foot of filtering surface can be safely figured as sufficient to filter 5 cubic feet of gas per minute without interposing serious resistance to the gas flow. As three filters are in series, this means that 15 cubic feet of gas per minute is actually being filtered through each square foot of each filter set.

DRYING THE SO₂ GASES.

The gases, after leaving the filters, go to a drying tower through a lead, steel, or even a wooden pipe. As there is no drop in temperature after leaving the filters there will be no further precipitation of sulphuric acid.

The drying tower (see fig. 24) is of cast iron, with closed top; a large flanged gas inlet enters the side of the tower close to the bottom at a downward angle so that none of the drying acid can run back into the gas-inlet pipe. The gas outlet is either in the top or in the side close to the top. A grill support of cast iron or acid-proof tile extends across the base of the tower above the top of the gas inlet; the incoming gases diffuse in the open space under the grill and rise through the tower. On top of this grill for a depth of several feet the tower is filled with special acid-proof distributing packing, or quartz pebbles 4 to 6 inches in diameter. Above this packing is a space of 8 to 12 inches and, if the tower be a side-outlet tower, the gas outlet is at this point. The tower wall is flanged at the top of this space, and on this flange rests another cast-iron section with upper and lower flange and with a solid bottom. In this bottom are bored countersunk holes; through each hole extends a porcelain tube of small bore and with a shoulder on one end, the shoulder

fitting down into the countersink in the iron bottom and being cemented in with acid-proof cement. The porcelain tubes should be of $\frac{1}{4}$ -inch to $\frac{3}{8}$ -inch bore and long enough to extend through the space below down into the quartz or tile tower filling. This upper section forms the acid distributing pan and is provided with a flanged acid inlet in the side. A flat cast-iron top covers the pan, being bolted to the top flange of the pan, and having a number of glass windows through which the operator may observe the acid in the pan below. These windows may be removed and the pan cleaned out or the porcelain tubes punched free from dirt if occasion arises. The acid for drying is a portion of the same acid that is used for absorbing the SO_3 . Acid is delivered to the drier by the same pump that delivers acid to the absorber, and the discharge from the drier goes to the same coolers that also serve the absorber. This is described in connection with the absorption system. Tests of the gas after leaving the drier permit the operator to regulate the amount of acid circulation necessary to dry the gas.

GAS BLOWER.

The gas is handled by means of a positive blower such as the Connersville or Root types. This blower should be of ample size and is usually driven by means of a variable-speed motor. It is advisable to cover the whole interior surface of the blower with a coat of heavy cup grease and to renew this covering every six months or every year.

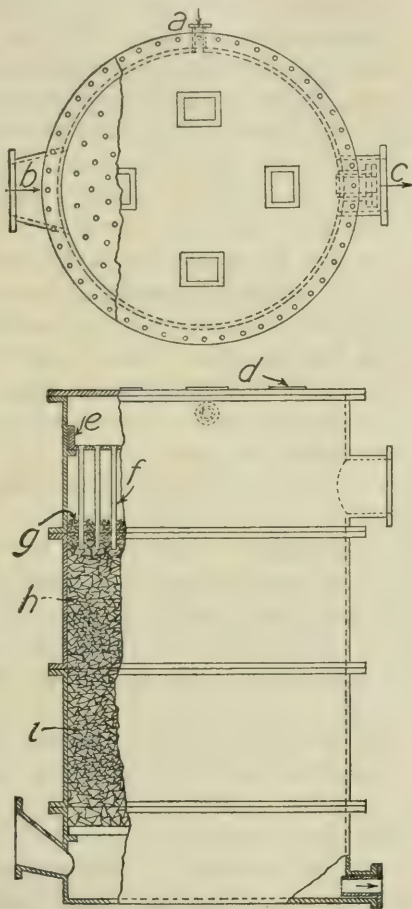


FIGURE 24.—Absorber and drier as used in the Badische system. *a*, Acid inlet; *b*, gas inlet; *c*, gas outlet; *d*, plate glass; *e*, pan; *f*, porcelain tubes; *g*, fine quartz; *h*, 3-inch quartz; *i*, 6-inch quartz.

GAS PREHEATING.

The gases from the blower enter the preheating furnace and are heated to reaction temperature which, as has been previously stated, is usually about 420° C. Preheating is usually done in vertical cast-iron U tubes about 4 to 6 inches inside diameter by 7 to 8 feet long. (Fig. 25.) The wall thickness of the preheating tubes is $\frac{3}{4}$ to 1 inch. The gases are delivered from a header into a number of these tubes in parallel; the tubes are connected in series with a considerable number of similar U tubes by means of cast-iron return bands. Flanged connections between the tube ends and the return bands are inadvisable, because the steel bolts of the connection would expand, causing gas leakage. A very good type of connection consists of casting a shoulder about 1 inch wide around the outside of the open ends of the U tubes (or, if the return bend is on the bottom, around the outside of the return-bend open ends) about $2\frac{1}{2}$ inches from the ends. A cast-iron ring about $1\frac{1}{2}$ inches larger in internal diameter than the outside diameter of the tubes is then set on this shoulder. This ring is about $\frac{3}{4}$ inch thick and about 5 inches high, and when set on the shoulder projects about $2\frac{1}{2}$ inches above the tube end. The open end of the return bend is then set down inside the ring and exactly on the tube end and the $\frac{3}{4}$ -inch space between the inside of the ring, and the outer walls of the tube and return bend is tamped full of a mixture of sal ammoniac and fine iron filings. This results in the formation of a so-called "rust joint," which is very strong and does not leak when heated. If the tubes have to be replaced, the cast-iron rings may be easily broken with a hammer and a new ring used, as the cutting out of such a rust filling with a chisel is very difficult and almost sure to break the ring.

The tubes are usually arranged with about twice as many in series as there are in parallel, therefore the containing furnace is rectangular in shape. (See fig. 26.) The vertical plane through the centers of the two arms of the U tube is not parallel to the side wall of the furnace but is usually at an angle with it, which staggers each row and assists in obtaining much better convection in the hot furnace gases. These furnaces should be fired with coal, coke, gas, or fuel oil. The flow of gases to be preheated should be countercurrent to the direction of the hot combustion gases passing through the furnace and around the outside of the tubes. The first row of tubes next to the fire should be protected somewhat from the direct impact of the flames by a fire-brick grill work or similar installation. A heat transfer of 1.5 B. t. u. per square foot per degree Fahrenheit difference per hour or 7.3 kg-calories per square meter per degree centigrade difference) is all that can be safely figured on for the exposed area of

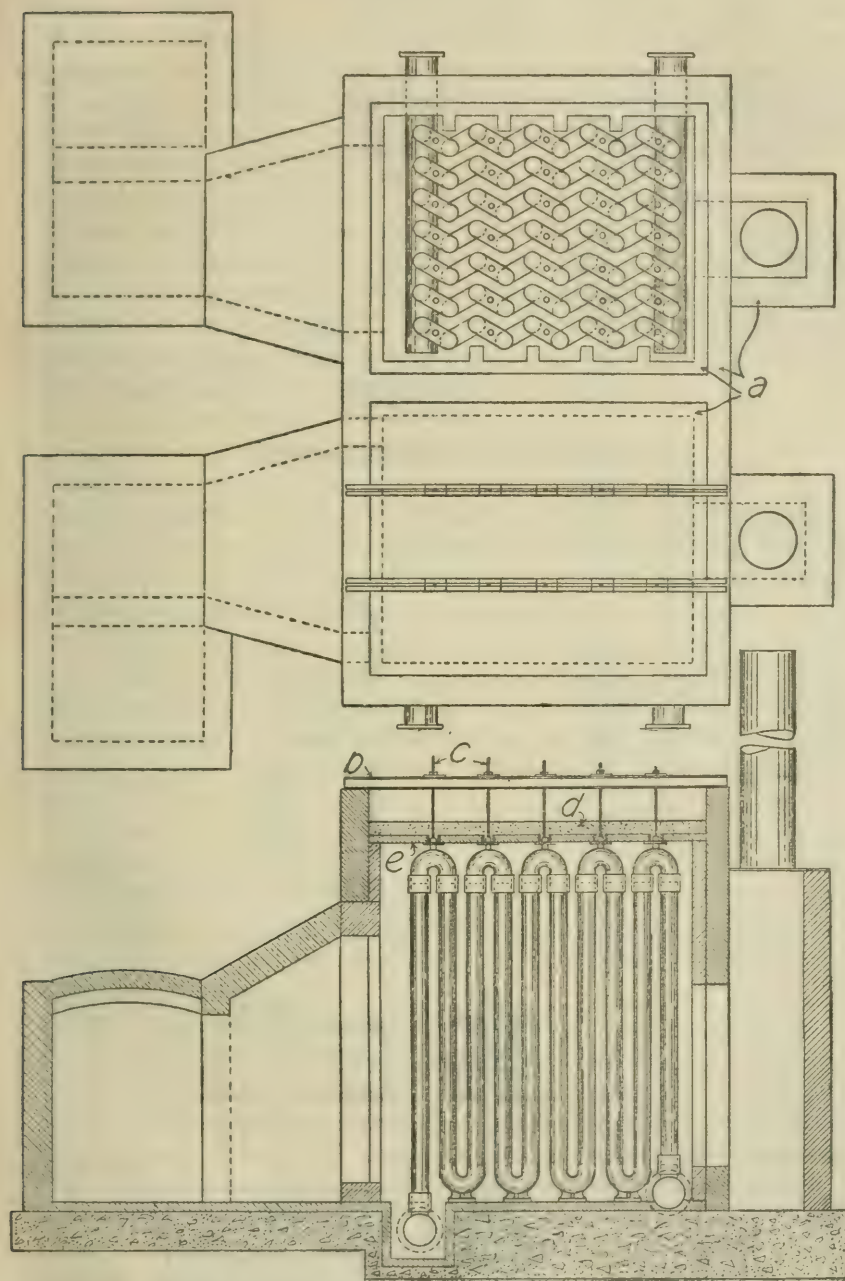


FIGURE 25.—Preheating furnace. Fire box shown is for crude-oil fuel. *a*, SO₃ gas inlet; *b*, six hundred 1½-inch boiler tubes, 10 inches long; *e*, SO₃ gas outlet; *d*, SO₃ gas outlet; *c*, SO₃ gas outlet.

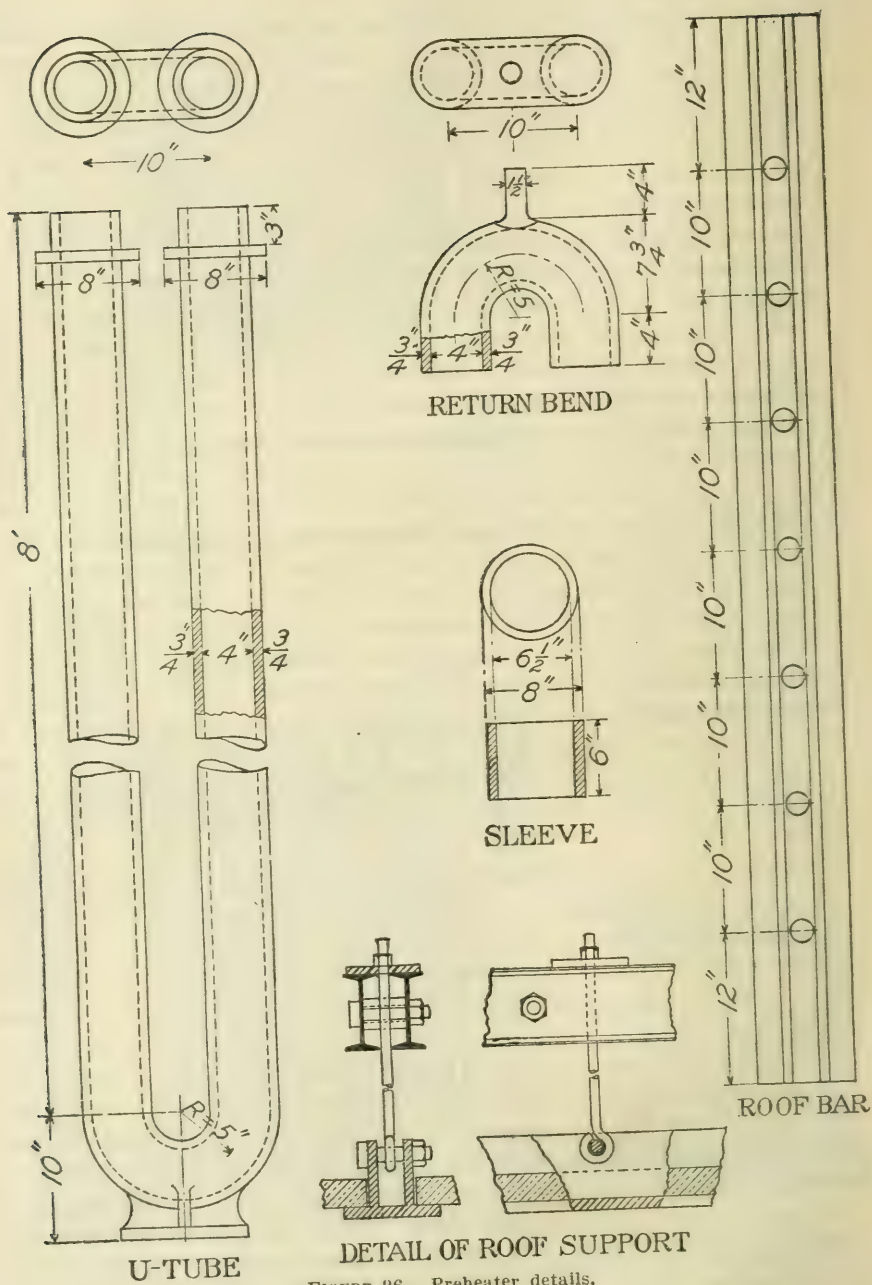


FIGURE 26.—Preheater details.

the preheating tubes. Ample tube surface should always be provided so that the tubes next to the fire will not have to be heated too high in order to obtain the required temperature of SO_2 gases, and also to utilize all the heat of the combustion gases. If properly designed and constructed, this type of preheating furnace will operate with very little trouble.

In a well-designed furnace, with gases averaging 6 per cent SO_2 by volume, the fuel consumption per net ton of H_2SO_4 produced varies between 550 pounds and 700 pounds of coal. With fuel oil a considerably higher efficiency may be obtained, and the amount of oil burned per net ton acid will vary from 1 barrel to $1\frac{1}{3}$ barrels. The fuel burned for preheating per ton of acid produced will vary, of course, according to the SO_2 content of the gas.

HEAT TRANSFER SYSTEMS.

The oxidation of SO_2 is an extremely exothermic reaction, and the heat thus generated in the converter is frequently utilized to preheat partly or completely to the reaction temperature the cold SO_2 gases entering the converter. This procedure has several distinct advantages, as follows:

1. Part or all of the fuel required for gas preheating is saved and this results in an important saving, both of materials and labor.
2. The danger of overheating the gases in the converter and consequent poor conversion is greatly minimized or done away with entirely.

3. Repairs on the SO_2 preheating installation are reduced to a minimum.

4. The hot SO_3 gases leaving the converter lose a large part of their heat to the entering cold SO_2 gases, thereby simplifying the problem of cooling the SO_3 gases before absorption and reducing the cooling equipment required.

One of the best systems of heat transfer used, especially in connection with the "Badische" process, involves the oxidation of the SO_2 to SO_3 in two steps by means of two converters in series, and the transfer of heat generated by oxidation in these converters into the incoming SO_2 gas by means of two exchangers in series. (Fig. 27.) The exchangers resemble surface condensers set on end, and are vertical steel cylinders with closed ends, each end being provided with a flanged opening for gas inlet or outlet. The tube sheets and the tubes are of steel; the two flanged openings are on opposite sides of the cylinder and close to the tube sheets. The tubes vary from $1\frac{1}{4}$ inches to $2\frac{3}{4}$ inches in diameter, and from 10 feet to 17 feet long, according to different conditions and designs.

The cold SO_2 gases enter heat exchanger 1 and are partly preheated, after which they pass to exchanger 2 in series, where the gases are preheated to their highest temperature. The gases then enter converter 1 where the SO_2 is partly converted to SO_3 with liberation of heat and consequent rise in temperature. The mixture of hot SO_2 and SO_3 gases then goes to heat exchanger 2, where the gases give up some of their heat to the incoming SO_2 gases. From heat exchanger 2 they pass to converter 2, where the oxidation to SO_3 is completed and the temperature again rises. The hot SO_3 gases from converter 2 then pass through heat exchanger 1 and give up heat to the cold SO_2 gases entering this exchanger. The SO_3 gases then go to the final cooling and absorption system.

This conversion and transfer of heat in two stages permits much better control of temperature than is possible when conversion is accomplished in one stage, and also prevents overheating in the converters. By-passes provided around the units of the system may be used to attain closer regulation if necessary. The entire installation, including both converters and heat exchangers, is thoroughly insulated in order to conserve heat. With this type of heat-transfer system, no auxiliary preheating is necessary after the first preheating in order to start the reaction; therefore, the preheating furnace is cut out of the system by means of a by-pass.

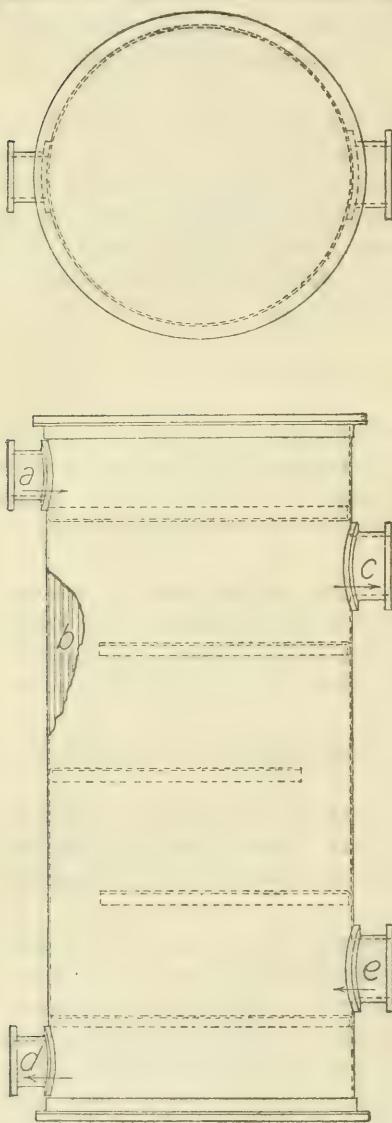


FIGURE 27.—Heat exchanger: *a*, SO_3 gas inlet; *b*, six hundred 1½-inch boiler tubes 10 ft. long; *c*, SO_2 gas outlet; *d*, SO_3 gas outlet; *e*, SO_2 gas inlet.

Another general scheme of heat transfer, used especially in connection with the "Mannheim" system, involves utilizing the heat from the SO_3 gases coming from the platinum-catalyzer shaft to preheat partly the SO_2 gases entering the shaft. This is done in an ex-

changer similar to that described in connection with the "Badische" practice. The SO_2 gases after leaving this exchanger are still further preheated in a system of large horizontal cast-iron pipes installed immediately over the arches of the oxide-catalyzer shafts. Then the gases are brought to the requisite temperature for reaction in the platinum-catalyzer shaft in a cast-iron preheating furnace similar to that previously described. However, as only a comparatively small boost in temperature is required after the gases leave the last exchanger, this final preheating furnace is comparatively small and the fuel consumption very low.

Another type of heat transfer, used especially in connection with the "Grillo-Schroeder" system, utilizes the heat of reaction from the converter to preheat the incoming SO_2 gases by passing them through an annular space between the converter shell and an exterior shell large enough to leave space for such gas passage. The details of the construction and operation of this type of heat transfer will be discussed in connection with the converter.

In another method of partial preheating, utilized especially by the "Tentelaw" process, heat from the reaction gases is radiated through a specially constructed cast-iron grill floor carrying the contact material up into the SO_2 gases entering above the grill floor. The details of the application of this method are discussed in connection with the converter as used in the "Tentelaw" process, on page 181.

In general, the statement may be made that it is feasible to utilize the heat generated by the oxidation of SO_2 to SO_3 to preheat partly or entirely the incoming SO_2 gases to a temperature at which oxidation by means of the platinum catalyzer will take place; that the extent to which such preheating may be carried depends upon the design and mechanical construction of the heat-transferring apparatus, and also upon the SO_2 concentration in the gases, which is an important factor in determining the maximum temperature attainable by heat transference.

GAS CONVERTERS AND CATALYTIC MATERIAL.

CONVERTERS CONSTRUCTED ON HEAT-TRANSFER PRINCIPLE AND USING PLATINIZED MAGNESIUM SULPHATE.

Figure 28 shows a combined converter and heat exchanger.

The converter has an outer shell 77 feet 4 inches in diameter by 13 feet 8 inches high, and a concentric inner shell 6 feet 6 inches in diameter by 12 feet 8 inches high, which is closed at the bottom by a dished plate, and fitted with an outlet 10 inches in diameter.

The inner shell is arranged to receive four separate layers of contact mass, each weighing 2,500 pounds and spaced at intervals of

2 feet 11½ inches. The mass is carried on perforated plates three-sixteenths of an inch thick; 8½ inches below each plate is fixed a cast-iron circular baffle plate with an open 5-inch space between the edge of the plate and the walls of the inner shell. The baffles serve to divert the gases, after each contact, to the walls of the inner shell, thus insuring desirable heat exchange with the gases circulating between the outer and inner shells.

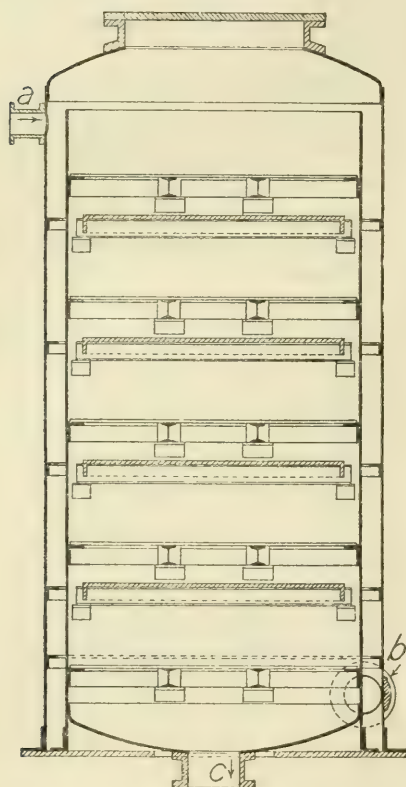


FIGURE 28.—Combined converter and heat exchanger used in "Grillo-Schroeder" system. *a*, SO_3 gases from preheater furnace, used in starting; *b*, SO_3 gases, cold; *c*, SO_3 gases.

The hot dry SO_2 -air mixture enters the outer shell tangentially, at the base, through 10-inch diameter inlet pipes and is compelled, by baffles, to circulate spirally in the space between the two shells, being heated by the gases inside the inner shell. Having arrived at the top of the inner shell, the gases first pass downward through a layer of un-platinized material, and then in turn through the layers of platinized material on the perforated plates below, being heated by the heat of conversion as each contact mass is passed through, and cooled as the corresponding baffle plate compels circulation along the sides of the shell. Finally the gases pass through the 10-inch outlet to the heat exchangers as already described and thence to the SO_3 coolers.

CONVERSION.

The essential conditions for good conversion—that is, 96 to 97 per cent efficiency—are briefly

as follows: (*a*) Careful operation of the burners and the supplementary air inlet in order to obtain a steady composition of the gases entering the converters; (*b*) efficiency in the purification system; (*c*) the maintenance of low temperatures in the converters, no temperature to exceed 480°C .; (*d*) the exit temperature of the gases leaving the converters should be about 410°C .; (*e*) all temperatures should be kept steady.

The temperature at which conversion commences is a function of the velocity of the gases, as is shown in the table following:

Relation of conversion temperature to velocity of gases.

Sulphur charge, pounds.	Velocity of gases, feet per second.	Temperature at which conversion of SO_2 to SO_3 starts, °C.
35	4.0	360-370
70	8.0	370-380
80	9.2	390-400

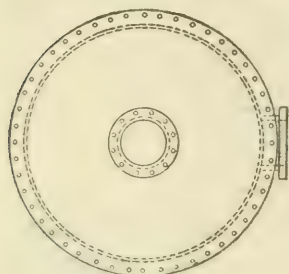
The converter temperatures must be carefully watched so that a uniform distribution of load is obtained, the maximum temperature at any point being 480° C. and the exit temperature within 10° of 410° C.

Temporary "poisoning" of the contact mass—such as is due to halogens—has the same effect as increasing the velocity of the gases, in that a higher temperature is required to start conversion. If the temperature can be raised quickly, temporary poisoning can be overcome, otherwise the poison must be removed by roasting the mass for about four hours with air at 450° C.

CONVERTERS CONSTRUCTED WITHOUT HEAT-TRANSFER PRINCIPLE.

A type of converter radically different from the one previously described in connection with the "Grillo-Schroeder" system is frequently used where the design calls for the preheating of the gas entirely by means of externally fired furnaces, or a separate heat exchanger, such as described in connection with the "Badische" system. This converter (fig. 29) consists of a cast-iron shell usually about 6 feet in diameter and 10 to 12 feet high, with a flanged gas inlet at the base and a flanged gas outlet in the dome cover at the top. Ribs are cast around the inside of this shell, which serve as bearings for the cast-iron grill floors or shelves. These shelves are usually spaced about 18 inches or 2 feet apart, and there are generally five shelves to each converter tube. About 1,500 pounds net dry weight of magnesium sulphate contact-material is placed upon each shelf, the coarsest material being spread over the shelf first, then a layer of the medium-sized material, and finally a top layer of smaller sized material. Pyrometer couples are placed over the shelves to indicate the rise in temperature taking place within, and the whole converter tube is insulated against too great heat loss, the amount of this insulation being determined by observation of temperature conditions after the unit is in use. The SO_2 gas enters directly from the preheating furnace or from the heat exchanger,

if one is used, into the base of the converter, passes upward through the catalytic material and is oxidized to SO_2 , the gases finally passing out at the top. There are usually two converters of this size, in parallel, to each unit, having a capacity of 18 to 20 tons H_2SO_4 per 24 hours, but some designers prefer to use smaller tubes (5 feet in diameter) and use four tubes to a unit.



PLATINUM CATALYZER WITH MAGNESIUM SULPHATE CARRIER.

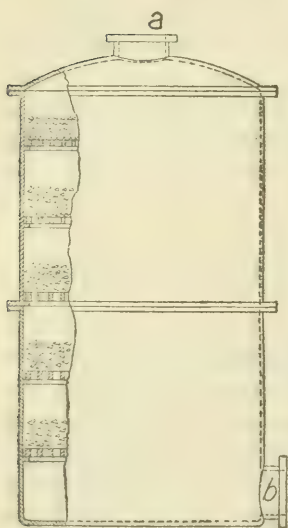


FIGURE 29.—Contact chamber as used in the Grillo-Schroeder system. *a*, Gas inlet; *b*, gas outlet.

The contact material used in the so-called "Grillo-Schroeder" system is platinum catalyzer with magnesium sulphate carrier. Magnesium sulphate, when properly calcined, has the property of forming a hard but very porous mass resembling pumice stone but more porous.

One method of preparing this type of contact material is as follows:

METHOD OF PREPARATION.

The magnesium sulphate crystals are first calcined in flat iron pans, 5 feet by 2 feet 9 inches by 3 inches deep, giving a cake, after baking, containing about 14 per cent moisture. This is passed through a Sturtevant crusher, set for the finest product, and then ground to dust (first dust) in a "devil" disintegrator, mixed with water and rebaked or recalcined in a hot pan of the same dimensions as the first.

The second cake is passed through a Sturtevant crusher, set for the coarsest product, and then through a rotating trommel screen, and graded as follows: (*a*) Dust; (*b*) dust under one-half inch; (*c*) "mass," from three-fourths inch to one-half inch.

The "mass" (grade *c*) is then stored, ready for platinizing, while grades *a* and *b* are passed through the disintegrator for the formation of dust (second dust) for rebaking.

The finished mass contains slightly more than 9 per cent water, and should be hard, resembling pumice stone in its tenacity, and having a vitreous fracture. A good test for the hardness of the mass is obtained by rubbing two pieces together. Good mass will resist the

friction and pressure, only giving a little surface dust and tending to become polished. It is extremely important that the mass should not be friable, as disintegration would result when the mass is introduced into the converter, and probably lead to loss of platinum, as well as causing increased resistance to the passage of the gases through the converter.

PRODUCTION OF THE FIRST CAKE.

The essentials for the production of a satisfactory first cake are as follows:

(a) The purest crystals only should be used, otherwise a porous cake will be produced.

(b) As soon as the contents of the pan have become solid, it must be frequently rubbed over to insure a compact mass.

(c) The normal time of baking is about seven hours, but prolonged heating does not affect the first cake adversely.

(d) The normal charge per pan is 200 pounds.

(e) The first dust must be as fine as possible, smooth to the touch, and free from unreduced grits.

PRODUCTION OF SECOND CAKE.

The essentials for the production of a satisfactory second cake are as follows:

(a) This should be made from equal proportions of the first and second dust.

(b) The charge per pan equals 140 pounds of dust, mixed into a thick cream with about $6\frac{1}{2}$ gallons of water. This gives a cake 1.1 inches to 1.3 inches thick.

(c) The mixing, with rakes, must be very thorough.

(d) The initial temperature of the pan must be such as to cause the mixture to boil freely, but not vigorously. If this condition is obtained and the mixing is carried out properly, the cake dries quickly without "explosions."

(e) The cake must be evenly dried and baked, and should be tested for hardness before removal from the pan.

(f) Each cake should be tested individually after removal and cooling and, if not a good sample, reduced to second dust for re-caking.

(g) The cake must be absolutely cold before crushing, if the maximum yield of correct size is to be obtained.

(h) The mass for platinizing should not be riddled for two or three days, as a good sample of cake becomes harder on storage. Bad mass, on the contrary, deteriorates.

PLATINIZING.

The mass is first carefully riddled over a $\frac{3}{4}$ -inch mesh screen to free it from dust. It is then placed in pottery trays on rubber mats in lots of 200 pounds; this quantity, with a moisture content of 9 to 10 per cent, is equivalent to 180 pounds of MgSO_4 . The amount of platinum chloride required to give an 0.3 per cent platinum content is then weighed out and dissolved in about $2\frac{3}{4}$ gallons of water. This is evenly spread over the mass, which is continually raked over to expose a fresh surface. A glass spray is used, and the head to produce spraying is obtained by raising the solution container to the necessary height by means of pulleys.

Heat is evolved during spraying and, after all the solution has been disposed of, the mass is allowed to remain for at least eight hours before being removed to the converters.

Another method of preparing the platinized magnesium sulphate mass, somewhat simpler and giving a more uniform platinum distribution but entailing a larger loss in platinum unless great care is used, is as follows:

The magnesium sulphate crystals are spread out in a steel pan about 4 feet wide by 8 feet long by 10 inches deep—about 1,000 pounds of the crystals being used for each pan charge. A very dilute solution of platinum chloride is then sprayed evenly over the whole exposed surface until the desired amount of platinum has been added. When this has soaked in, the moist mass of crystals is thoroughly mixed by means of shovels. The impregnated mass of crystals is then shoveled onto the tile hearth of a furnace. This furnace (fig. 30) is constructed so that the products of combustion pass under the tile hearth, then up over a bridge wall, back over the mass of crystals on the hearth, and, finally, out of a stack. The hearth is usually about 4 feet wide by 10 feet long. In one side three wide doors are provided, through which the material is shoveled in and raked out and through which the charge is spudded and rabbled. The base of these doors is on the same level as the hearth; a shelf about 1 foot wide extends along the outside of the furnace, also at the hearth level.

Every endeavor is made to have a neutral or reducing flame in firing the furnace, especially on the first cooking of the platinized crystals.

The tile hearth should be hot (300° to 400° C.) when the crystals are shoveled in. The door exits should be dammed to a depth of 6 or 8 inches with fine, previously calcined material and the doors shut at once in order to keep out all excess oxygen.

The magnesium-sulphate crystals melt in their own water of crystallization, and as this water is evaporated off the whole mass swells

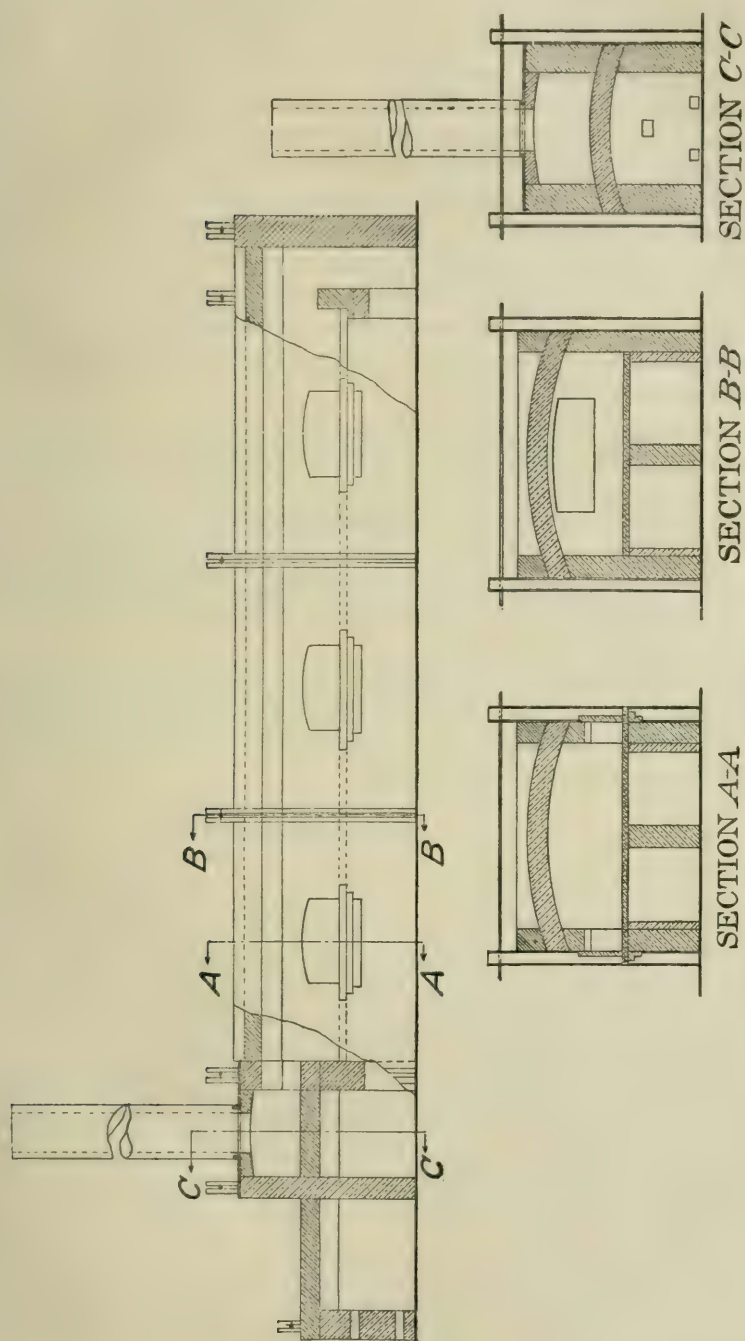


FIGURE 30.—Furnace for calcining magnesium sulphate contact material.

up in a porous, moist cake. When this condition is reached a strong crust has been formed next to the hearth, and at this point the cake should be broken up and turned over by means of a wide, flat-nosed steel spud driven in between the tile hearth and the hard crust on the underside of the cake. The large chunks are then broken up and turned over from time to time until all the moisture is evaporated except the last molecule of the water of crystallization. The cake is then raked out and cooled. After cooling it is ground through close-set fluted rolls or in a grinder. Care must be taken to avoid dust loss. The ground product is then remixed with enough water to make a thick paste and allowed to set until it solidifies. It is then reroasted in the same manner as before, except that the hearth may be a little hotter to start with and such great care need not be taken to maintain reducing conditions.

The cake from the second roasting is run through a pair of fluted rolls set about three-fourths of an inch or 1 inch apart. The crushed product is then sized through a set of shaking slotted screens. Four sizes of final product are obtained: (1) Through $\frac{1}{4}$ -inch by $\frac{5}{8}$ -inch slots—fines which are crushed and refurnaced; (2) through $\frac{1}{2}$ -inch by $\frac{3}{4}$ -inch slots, on $\frac{1}{4}$ -inch by $\frac{5}{8}$ -inch slots; (3) through $\frac{3}{4}$ -inch by $1\frac{1}{4}$ -inch slots on $\frac{1}{2}$ -inch by $\frac{3}{4}$ -inch slots; (4) through 1-inch by $1\frac{1}{2}$ -inch slots on $\frac{3}{4}$ -inch by $1\frac{1}{4}$ -inch slots.

There is no oversize, as it is spalled on the top screen until it passes through the 1-inch by $1\frac{1}{2}$ -inch slots. The finished material is put into closed bins, each size being in a separate bin, and is kept there until it is placed in the converter.

AMOUNT OF CATALYTIC MATERIAL REQUIRED.

A wide divergence is found in different plants as to the quantity of platinum required to oxidize a given quantity of SO_2 gas and also the quantity of carrier necessary for such platinum, or in other words, the platinum concentration of the contact mass. As a matter of fact, there are many features which radically influence capacity. Principal among these may be mentioned:

1. Absolute cleanliness of the gas, not only from mechanical impurities, but also from gaseous impurities, especially the halogens, AsH_3 , and similar gases. The presence of any of these impurities will interfere with conversion and cut down the capacity decidedly.

2. Porosity of platinum carrier or actual surface exposure for a given weight of platinum used.

3. Concentration of SO_2 in the gases and efficiency of conversion desired. A large increase in the amount of SO_2 oxidized by a given weight of platinum is possible if the cost of sulphur dioxide is not a large factor, and high conversion and consequent high yield from sulphur is not an essential.

4. Fairly accurate control of heat conditions within the converter in order to avoid too high temperatures with consequent inhibition of the oxidation or reversal of the reaction.

In general, it may be stated that, with very efficient operation, using absolutely clean sulphur dioxide gas at a concentration of 6 to 7 per cent SO_2 along with the carefully prepared, very porous, magnesium sulphate contact material, and with proper control of temperatures the average practice in the United States uses 14 to 16 Troy ounces of platinum for each ton of H_2SO_4 (monohydrate basis) daily production. Plants are now in operation using only 12 ounces of platinum per ton of H_2SO_4 production.

As regards the platinum concentration in the contact material, this varies from 0.1 to 0.3 per cent by weight, but the evidence is not conclusive that either of these extremes is preferable, as the porosity and consequent surface exposure of the platinum carrier varies greatly. It has frequently been found advisable to fill the converter with contact material of several different platinum contents, using material of 0.1 per cent content for the initial oxidation and finishing with material of considerably higher platinum content.

TREATMENT OF FOUL MAGNESIUM-SULPHATE CONTACT MASS TO REVIVE ITS ACTIVITY.

If the loss of activity is due to temporary "poisoning," such as is caused by the presence of halogens, the cause of the trouble—that is to say, the poisonous gases—should be first corrected, after which raising the temperature of the incoming gases will frequently increase the conversion to its original efficiency. If this be done the temperature must be lowered very slowly to its original point, and sometimes must be maintained at 5° or 10° C. higher than the original point.

If the poisoning is more serious, caused by traces of arsenic or other similar compounds, this condition can be largely overcome by shutting down the converter while hot and immediately filling it with chlorine gas, blinding the inlet and outlet of the converter, and permitting the contact mass to stand, heated, in the atmosphere of chlorine for about 24 hours, when the converter should be again cut into the system and brought up to the required temperature by passing hot SO_2 gas through it. Within 18 to 24 hours after the SO_2 gas is introduced good conversion is usually obtained: if the poisoning has not been too serious, the conversion efficiency will be nearly that of the new, clean material.

If the poisoning is very serious, caused by large amounts of arsenic, SiF_4 , or other impurities, the contact material must be taken out of the converter, treated, and reroasted. The method of treatment is as follows:

Into a rectangular wooden box, about 4 feet wide by 10 feet long by 12 to 14 inches deep, should be placed enough pure water to add about 5 molecules of water to the amount of foul magnesium sulphate material to be treated. Into this water should be dumped about 25 gallons of strong nitric acid and $12\frac{1}{2}$ gallons of commercial muriatic acid. One thousand to 1,200 pounds of the foul contact material should be then gradually dumped into the weak acid mixture. This must be done carefully, as a great amount of heat is generated and the solution is liable to foam and boil over, causing a heavy loss in platinum. Generally about half of the charge of foul material is added and stirred thoroughly until the reaction has subsided, after which the balance of the material is added in smaller lots, the mixture being stirred after each addition until the reaction has subsided.

The dehydrated magnesium sulphate goes into solution with difficulty, but the temperature of the solution rises very considerably and by suitable and continuous stirring all of the magnesium sulphate may be dissolved. The addition of 25 to 50 pounds of cane sugar to the batch is advisable, as this sugar not only assists in the subsequent "setting" of the batch but also acts as a reducing agent to facilitate reduction of platinum in the subsequent calcining. After the charge is completely dissolved it should be allowed to stand until the whole mass has solidified, which usually takes about 24 hours. It is then broken up, removed from the box, and roasted, screened, and sized in exactly the same manner as with new material, except that complete grinding of the first roasted product is unnecessary.

A simple method of testing contact material to determine whether it is active is to hold a small piece with a pair of tongs in the flame of an ordinary Bunsen burner until it is incandescent; then pinch the gas tube of the burner putting out the flame, until no incandescence is visible in the piece of contact material; release the tube, allowing the gas to again come from the burner, and if the contact material is active the gas will ignite. This is a rough method, but quick, and gives an extremely good index as to the activity of the mass.

PLATINUM CATALYZER WITH ASBESTOS FIBER CARRIER.

The type of contact material used in the "Badische" process is platinum catalyzer with asbestos fiber carrier. The material consists of carefully selected long-fiber asbestos treated in somewhat the same manner as is described later in the discussion of the treatment of the asbestos used to make the mats in the "Mannheim" process. After the asbestos fiber has been treated and dried it is immersed in a bath of platinic chloride; the impregnated asbestos is permitted to drain,

dried, and fluffed. This asbestos is then placed upon grided shelves in cast-iron converters, so connected that the gas flow is downward, in order to keep the light, fluffy material in place and prevent channeling. Usually two converters are used to each unit in connection with two external tubular heat exchangers, such as have been previously described. The first converter is considerably larger than the second converter, and most of the conversion takes place in the former. The asbestos in the second converter usually carries a higher platinum content than that in the first converter, but there is less material used. This contact material gives the largest surface in proportion to the platinum used of any of the various catalytic materials, and for that reason less platinum is required per ton of acid capacity than is required in the best type of magnesium sulphate-platinum contact material. Very good results are obtained on a basis of 13 to 14 Troy ounces of platinum per ton daily capacity of monohydrate sulphuric acid.

The success of this form of catalytic material depends upon the absolute cleanliness of the gas from mechanical impurities, acid mist, etc. Temporary "poisoning" by halogens may be overcome in the same manner as with other materials, but retreatment of this material when it is badly fouled with arsenic or other similar "poisons" is practically impossible. If this contingency arises, it is necessary to replace with new contact material and recover the platinum from the old material. The asbestos fibers, being extremely fragile, will not withstand anything but the most careful handling, and rapidly lose their strength and stability when exposed to the high heat inside of the converters.

CONVERSION SYSTEM OF THE "TENTELEW" PROCESS.

In the "Tentelaw" process the preheating of the incoming SO_2 gases and the maintaining of uniform temperature within the converter are largely accomplished by an entirely different method than is employed in any of the other processes—namely by heat radiation instead of by heat transfer. The cold incoming SO_2 gases first pass through a single vertical tubular heat exchanger (fig. 31), constructed after the same design as has been previously mentioned in connection with the "Badische" process, but the increase in temperature is much less than in the "Badische" or "Grillo-Schroeder" heat transfers. The partly preheated gases, after leaving the heat exchanger, enter the top of the converter (fig. 32). The converter is constructed so as to utilize heat by radiation and also to take advantage of the fact that with gases moving at very slow speed the platinum catalyzer becomes active at a much lower temperature than is ordinarily the case. The top part of the converter is, rela-

tively speaking, very large, hence the velocity of the entering gases is greatly reduced. This part of the converter, with very large cross-section, is termed the "equalizing space"; at the bottom of this space is a specially constructed cast-iron grill or sieve-plate. This sieve-plate is provided with a large number of cast-iron "pyramids" projecting upward. The principal portion of the contact mass, which is platinized asbestos, is spread on this sieve-plate but

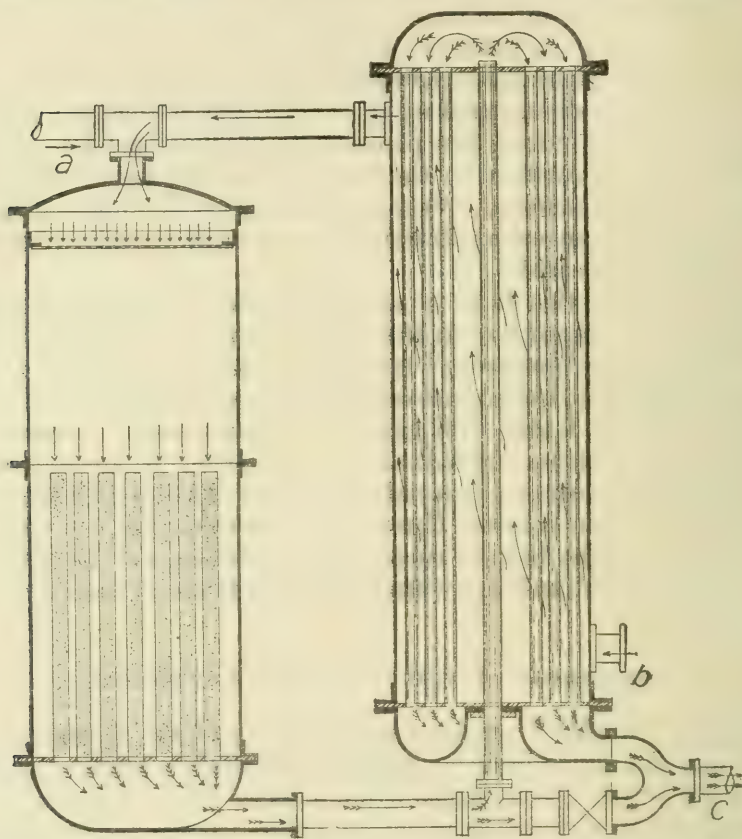


FIGURE 31.—Heat exchanger and converter, "Tentel" system. *a*, inlet used in starting; *b*, inlet to preheater; *c*, outlet.

does not reach completely to the top of the pyramids. As this upper portion of the contact mass that comes into contact with the fresh gases has a large surface exposure it radiates a considerable amount of heat into the equalizing space above it. Radiation is also greatly assisted by the cast-iron pyramids conducting heat from their bases, which are surrounded by active contact mass, to their points, which protrude above the mass and into the gases entering it. By this means not only are the gases entering the contact mass preheated

to a temperature at which maximum oxidation takes place, but this transfer of heat also serves to cool the temperature of the gases in the zone of reaction itself, and thus prevents serious overheating of the platinum catalyzer. After passing through the sieve-plate the gases enter a part of the chamber which has a much smaller cross section, this part containing the rest of the contact material and being heavily insulated to prevent loss of heat. The final oxidation takes place here and the hot SO_3 gases pass out at the bottom and into the top of the tubular heat exchanger previously mentioned, preheating the entering SO_2 gases to a temperature sufficiently high to start the reaction when reinforced by the additional heat radiated from the sieve-plate. An external preheating furnace with by-pass connections is used to start the process, then this furnace is cut out and the operation proceeds as described.

COMBINED OXIDE AND PLATINUM SYSTEM.

Some systems, especially the "Mannheim," economize in the use of platinum by utilizing hot ferric oxide to oxidize part of the SO_2 , the oxidation being completed by means of platinum. The ferric oxide is a product of the roasting of coarse (2-inch to 2½-inch) pyrite in lump burners. This product is screened after being discharged from the lump burners and the coarse oxide is used in the oxide shafts.

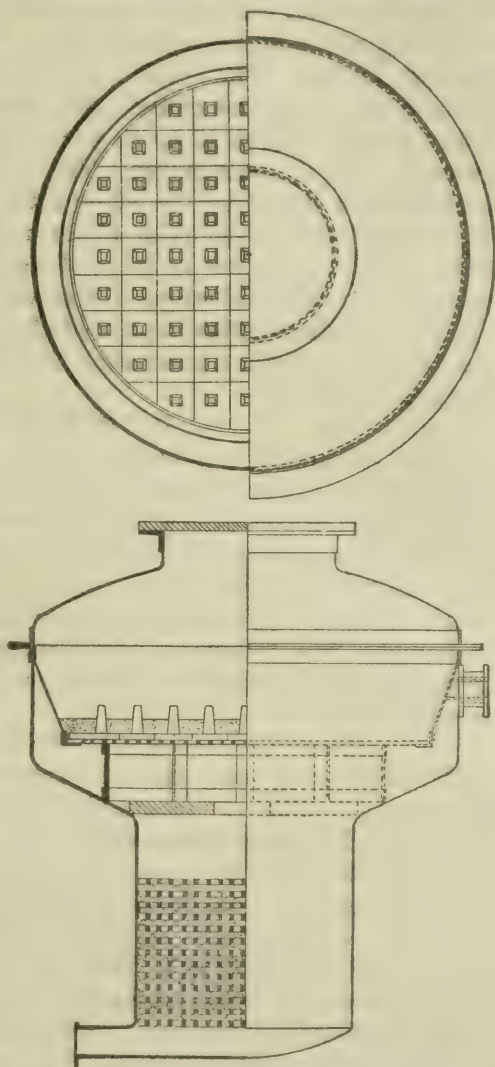


FIGURE 32.—Combination converter and heat exchanger, "Tentelw" system.

OXIDE SHAFTS.

These shafts are usually square, steel, brick-lined chambers measuring 20 to 25 square feet in cross section and 10 to 12 feet high. They are filled with the burned, screened, iron-oxide lumps, 2 inches or larger in size. A certain amount of fresh oxide lumps is added to the top of the shaft each day and a corresponding amount drawn from the bottom. The hot SO_2 gas mixture from the ore or sulphur burners enters the base of the oxide shaft and passes up through the oxide filling. About 40 to 50 per cent of the SO_2 is usually converted to SO_3 in these towers. The temperature of the ferric oxide contact mass should not be below 600°C. , otherwise SO_3 is lost, as it combines with ferric oxide to form ferrous sulphate. The mixed SO_2 and SO_3 gases are cooled and the SO_3 absorbed in strong sulphuric acid; the residual gas is filtered and cleaned, passed through the heat transfers following the platinum shaft and above the oxide shafts, then through a preheating furnace, and, finally, through the platinum shaft.

PLATINUM SHAFTS.

There is usually one platinum shaft to each two oxide shafts. Each shaft usually consists of three ovens about 4 feet square by 1 foot deep. In each oven are placed several platinum mats supported between wire gauze. The mats are made of about $\frac{3}{4}$ -inch asbestos rope woven with the strands about one-eighth inch apart in the clear. From 20 grams to 25 grams of platinum are deposited on each mat. The following is a description of the Mannheim mat platinizing and mounting process, which is typical of the usual practice:

METHOD OF PLATINIZING AND MOUNTING THE MATS.

To 40 liters of pure distilled water is added 1 liter of a solution of sodium carbonate (containing three-eighths of a pound of Na_2CO_3). The liquid is heated by means of steam at about 20-pound pressure until it boils vigorously; then the asbestos mat, which has been shaken to remove loose particles, is placed in the bath. One liter of sodium-acetate solution (containing 1 pound of pure HCOONa) is added, and, after bringing the liquid again to the boiling point, 400 cubic centimeters of 10 per cent platinic chloride (PtCl_4) solution (previously made alkaline with sodium-carbonate solution) is poured in slowly. The mat is moved up and down through the solution three or four times, and then a cover is placed on the bath and the liquid allowed to boil for a quarter of an hour. The mat is then reversed and a further 200 cubic centimeters of platinic chloride (PtCl_4) solution added, after which the solution is kept at the boiling point until the whole of the platinum has been deposited on the mat. This takes 10 to 20 minutes, and is shown by the complete clearing of the liquid.

The mat is then reversed and placed in another bath containing 50 liters of cold water. When 10 mats have stood in this bath 4 to 6 hours, the water is run off and replaced by 60 liters of a 10 per cent H_2SO_4 wash at a temperature of 35° to 40° C. This first acid wash lasts about 18 hours, and is followed by a second 10 per cent H_2SO_4 wash, lasting the same length of time and at the same temperature.

The acid treatment is followed by two hot-water washings, each lasting 10 to 12 hours, which remove the soluble sulphates formed during the treatment with H_2SO_4 .

The mats are then placed on wooden racks in a hot-air oven, at a temperature of about 60° C., to drain and dry. After drying, they are ready to be mounted for baking in the platinum shaft. The mats are mounted as follows: (a) Heavy iron frame with handle, (b) iron-wire grid, (c) platinized mat, (d) light iron frame, and so on until 10 mats are in position.

The complete element is now placed in one of the sections of the platinum shaft and baked for 5 to 6 hours at a temperature of 450° C. After baking, the element is dismantled and the mats placed carefully (as they are very brittle) in a tank filled with cold distilled water, where they are left for about 2 hours, until they are quite pliable. The water is then run off and a 10 per cent solution of hydrochloric acid is added and kept, by means of steam, at about 50° C. for 12 hours.

After this follow two hot-water washings, each lasting 6 hours, and finally one cold-water wash lasting the same length of time.

The mats are then drained on racks and sprinkled with cold distilled water until the water draining from the mats shows no trace of either chloride or sulphate. The mats are then drained and dried and are ready for use.

It is important to test the distilled water systematically, as the presence of any impurity affects the deposition and adherence of the black platinum on the asbestos.

RE-TREATMENT OF MATS FOR REMOVAL OF ARSENIC.

After the removal of an element from the plant, samples are taken from the third and sixth mats, and the percentage of arsenic determined. The mats are then given a 5 per cent hydrochloric-acid wash at 60° C. for 6 hours. They are then washed twice in hot water and finally drained and sprayed with distilled water till the water issuing from the mats shows no trace of sulphate or chloride. The mats are then dried and samples again taken to determine the arsenic content in the re-treated mat.

The two-stage system of oxidation with ferric oxide and platinum, of the Mannheim process, is considerably more expensive both in instal-

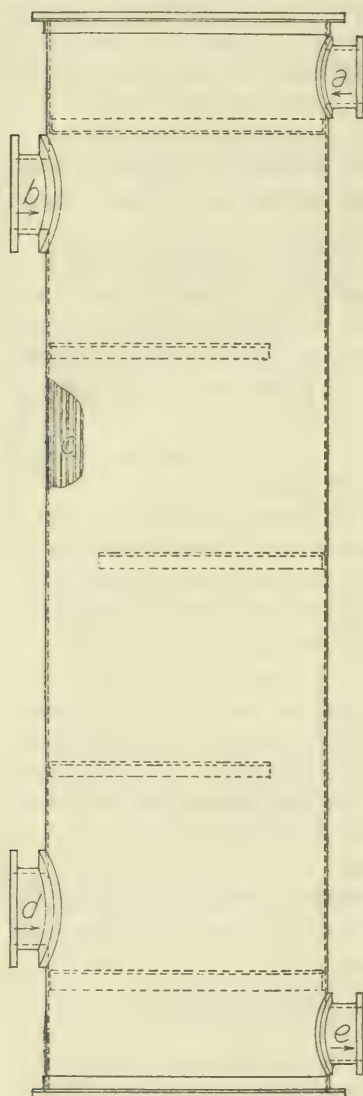


FIGURE 33.—Natural-draft air cooler for cooling SO_3 gases after leaving the converter. *a*, SO_3 gas inlet; *b*, air inlet; *c*, six hundred boiler tubes, $1\frac{1}{2}$ inch by 18 feet; *d*, air inlet; *e*, SO_3 gas outlet.

lation and operation than any of the "straight" platinum oxidation systems. The multiplicity of heat transfer systems, SO_3 absorption systems, oxide and platinum converter units, etc., add greatly to the initial installation cost and complicate the plant operations, repairs are a heavy expense item, and the only advantage is a saving for platinum in the original installation. An advantage of the ferric oxide contact shaft is that it removes the arsenic effectively and thus protects the platinum mass.

COOLING THE SO_3 GASES.

The SO_3 gases, after leaving the converter or heat transfer, are passed through a cooling system before they enter either the oleum towers or the final absorbing tower. This cooling system usually consists of simply steel or cast-iron pipe, air cooled, of sufficient size to carry the gases without frictional resistance and long enough to cool the gases by radiation to a temperature of 50°C ., or preferable lower (fig. 32).

If the SO_2 gases, before conversion, have been thoroughly dried with strong sulphuric acid, there will be no acid condensation in the cooling system following the converters, and steel piping may be used. This pipe may also be water sprayed if desired. If the gases, however, contain a considerable amount of H_2SO_4 after conversion, this acid will precipitate out as the gas cools, and

cast-iron pipes must be used for the first (hot) portion of the cooling installation, as hot, strong H_2SO_4 attacks steel. Steel heat transfers can not be successfully used unless the gases are thoroughly dried.

Cast-iron pipe cracks badly, however, even when cast without chaplets, and, from every consideration, it is advisable to dry thoroughly the SO_2 gases before conversion.

FINAL ABSORPTION SYSTEM.

The final tower in which the SO_3 is absorbed in sulphuric acid is constructed exactly like the tower for drying the SO_2 gases, previously described. The acid delivered to the distributing pan at the top of the tower should be in such quantity relative to the SO_3 to be absorbed that the acid will be strengthened from 97 or $97\frac{1}{2}$ per cent entering strength to 99 or $99\frac{1}{2}$ per cent exit strength in its passage through the absorbing tower and at the same time absorb all the SO_3 .

The acid, after leaving the base of the absorbing tower, passes through a cast-iron pipe to an acid cooler situated off to one side and at a lower level. In this pipe, and close to the tower, is provided an overflow through which all the acid not returned from the cooler to the absorbing tower passes. This acid is the plant product and goes to storage or direct to the oleum system. The strength of such acid is usually about 99 or $99\frac{1}{2}$ per cent.

Between this overflow and the cooler is situated the weak acid or water inlet where the requisite proportion of water is added to reduce the acid to about $97\frac{1}{2}$ per cent strength. At this point, also, the acid returning from the SO_2 drier enters.

The adding of the weak acid, the drying of the SO_2 gases in the drying tower, and the absorption of the SO_3 in the absorbing tower all tend to raise the temperature of the acid, and this temperature must be reduced by cooling.

The acid-cooling system is of cast iron and may be simply large pipes, water sprayed, or, more preferably, a manifold cooler built of sections of standard pipe and fittings in such a manner that the acid to be cooled passes between an outer and inner pipe, the inner pipe being water cooled. (See fig. 34.) Provision should be made for draining and cleaning the cooler occasionally, as sulphates tend to accumulate.

From the cooler the acid is delivered to the pans of the absorbing and drying towers by means of a cast-iron centrifugal pump. This pump should be a closed runner pump, designed in such a manner that the stuffing box is on the suction side. A vertical pump with long shaft, acid inlet around the shaft above the runner, and long pipe section between the acid inlet and the stuffing box above works very well. If well designed and constructed, such a pump will run for a year or more without repairs.

OLEUM SYSTEM.

In the manufacture of oleum (fuming sulphuric acid) part or all of the strong acid overflowing from the absorbing tower is passed down through towers against an upcoming stream of SO_3 gases.

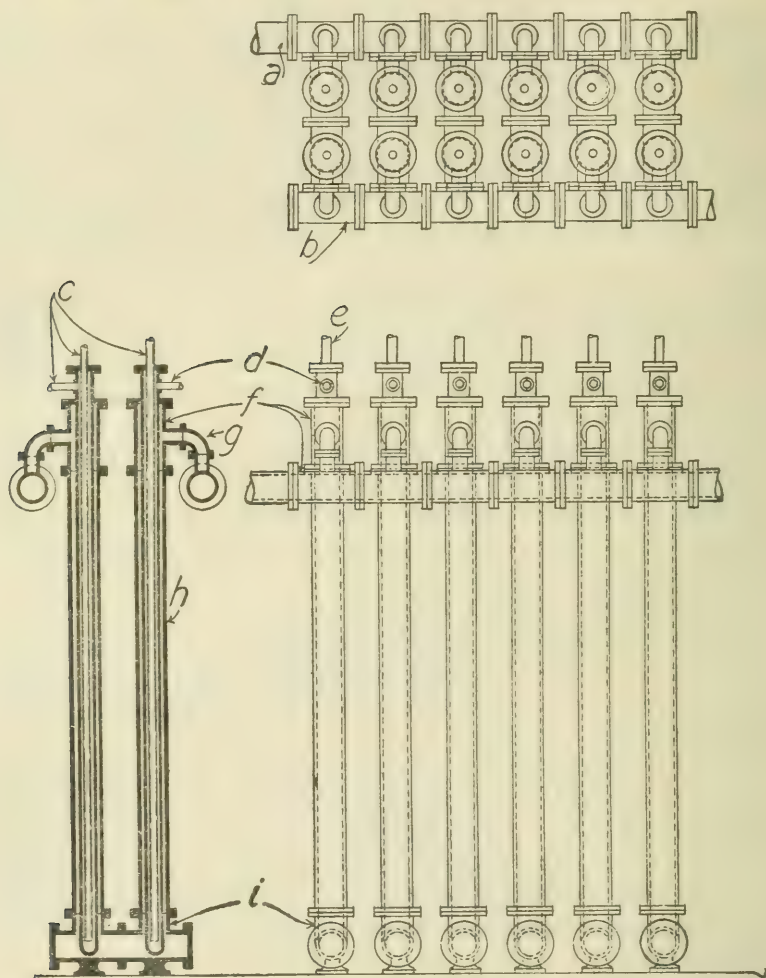


FIGURE 34.—Cooler for strong acid. *a*, Acid inlet manifold from absorber; *b*, acid outlet manifold; *c*, standard 1-inch pipe; *d*, cooling water outlet; *e*, cooling water inlet; *f*, standard tee, 6 inches by 6 inches by 12 inches; *g*, standard 2-inch ell; *h*, standard 6-inch cast-iron pipe; *i*, standard 6-inch base tees.

These towers may be 15 to 30 inches inside diameter and 10 to 25 feet high, depending on the capacity desired and the strength of the SO_3 gases. Hot oleum attacks steel and also tends to crack cast iron. An excellent type of construction comprises an outer steel shell with cast-iron base and top. This steel shell is lined with thin

cast-iron liner rings or sections, the small space between the rings and the outer steel wall being filled in with a semifluid acid-proof cement, such as sodium silicate and silex, which hardens under the action of the acid.

The towers are filled with large quartz pebbles or special acid-proof filling in order to provide a large absorption surface. As the absorption of SO_3 by sulphuric acid generates heat, a small acid cooler should follow each oleum tower if these towers are arranged in series. Cast-iron or steel tower shells lined with acid-proof brick (fig. 35) are also used successfully, but have the disadvantage of poor heat radiation.

There are several methods of arranging and operating these towers.

Several towers may be installed in parallel, all supplied with SO_3 gases from a common header and the amount of gases entering each tower from the header being controlled by a valve. The strong acid from storage is admitted into the top of each tower; the oleum discharges at the bottom of each tower through a hydrometer boot. In this way the strength of the oleum produced in each tower may be closely governed by regulating the gas and acid flow. The gases and SO_3 from the oleum tower go directly to the 97½ or 98 per cent acid towers for complete recovery of the SO_3 .

Another method is to have two or more oleum towers in series directly in the gas line leading from the converters or heat transfers to the absorbing tower. In this installation all the SO_3 gas passes through the oleum towers in series. The strong sulphuric acid passes down through the towers in series, and acid coolers (fig. 36) are installed between each two oleum towers. In this type of installation the strength of the oleum is regulated solely by control of the amount of acid absorbed and the temperatures, as all the gas is

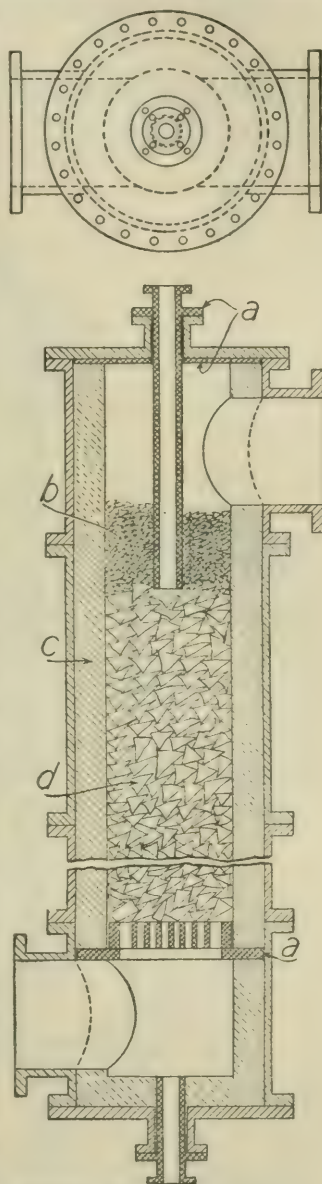
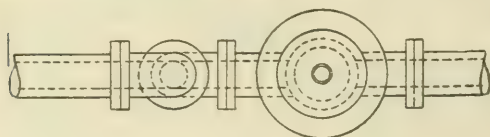


FIGURE 35.—Oleum tower. a, Tantalum; b, 3-inch quartz; c, duro brick laid with duro cement; d, 4-inch quartz.

passing through the towers at all times. If the oleum produced is too strong, it is weakened by admitting weaker acid after the last absorption of SO_3 has taken place.



APPROXIMATE INSTALLATION AND MANUFACTURING COSTS.

COSTS OF INSTALLATION.

The costs of installing the Grillo-Schroeder, Badische, or Tentelew systems in a fairly large-sized plant (daily capacity 60 tons or more) do not differ widely. On a prewar basis, with costs of material and labor as in about the years 1910-1914, the cost would be approximately \$6,000 per ton of H_2SO_4 (100 per cent basis) daily capacity if pyrite burners and complete ore-handling equipment be included.

The substitution of sulphur for pyrite would decrease the installation cost \$1,000 to \$1,500 per ton of daily capacity.

The cost of materials and labor existing in this country during the war and at the present time are so much higher than in prewar times and vary so widely that a general estimate of present costs of installation is liable to be misleading.

The following estimates per ton of daily-capacity installation cost cover a large plant construction in

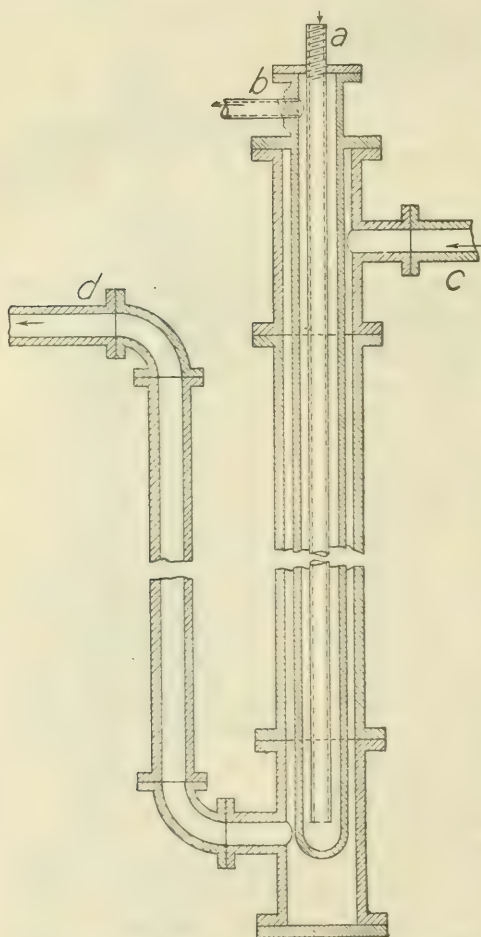


FIGURE 36.—Cooler for acid from oleum towers.
a, Cooling water inlet, 1-inch standard pipe;
b, cooling water outlet; c, acid inlet; d, acid outlet.

the United States during the year 1918 and utilizing brimstone as the sole source of SO_2 gases. This plant used a modification of the Grillo-Schroeder system.

Estimated cost of installing a large acid plant in 1918.

General:	Per ton, daily capacity.
Excavation.....	\$40
Miscellaneous.....	80
Total.....	120
Buildings:	
Concrete.....	286
Structural steel.....	352
Lumber.....	240
Tile.....	48
Roofing (all classes).....	108
Total.....	1, 154
Equipment:	
Material.....	3, 314
Labor.....	1, 700
Total.....	6, 168
Platinum.....	1, 560
Total.....	7, 728
Overhead, supervision, and indirect expense.....	600
Grand total.....	8, 328

The estimates for this plant, however, also included several denitrating and heat concentrating towers, very large acid storage tanks, and all accessories. No heat transfers were used.

For a Grillo-Schroeder unit of approximately 20 tons daily capacity, including dust flue, cooling and scrubbing system, box type filters, preheating furnace, contact tubes, gas cooling and absorbing system, oleum system and acid storage, but not including roasting or ore handling installation or buildings, the approximate amount of materials required is as follows:

Materials required for a Grillo-Schroeder unit of 20-ton capacity.

Brick.....	26, 000
Concrete, cubic yards.....	225
Lead, pounds.....	82, 000
Cast iron, pounds.....	215, 000
Steel, pounds.....	45, 000
Lumber, board feet.....	45, 000

As the size of plant increases up to about 60 tons daily capacity, the ratio of construction materials used to tonnage capacity decreases materially. The amount of buildings necessary depend largely upon the climatic conditions at the plant locality.

The cost of a Mannheim-type plant, with its double oxidation and absorption system, is much higher than that of any of the other three types of plants mentioned.

MANUFACTURING COSTS.

The factory cost of producing sulphuric acid in this country prior to the war in large and well designed plants of the Grillo-Schroeder, Badische, or Tentelaw systems, including plant overhead charges, cost of ore roasting and all charges for operation and repairs, labor, and materials, but not including plant amortization or cost of sulphur, varied between \$2.50 and \$4 per ton of acid (100 per cent H_2SO_4 basis). This range in costs arises from variations in the gases used as to SO_2 strength and dust and fume content; from the complete or partial use of heat transfers for gas preheating, or the absence of such equipment, necessitating preheating by fuel; and lastly, but not least, from intelligence in the design and operation of the plant.

The following estimates of actual cost of operation apply to a plant constructed during 1918.

Estimated cost of operation, per ton of acid.

Coal consumption, tons-----	0.33
Water consumption, gallons-----	6,900
Power consumption, horsepower-hours-----	120
Compressed air, cubic feet:-----	2,000

The number of men required to operate a contact plant is comparatively small. For a plant ranging up to 60 tons in daily capacity one operator per shift with an assistant, who also attends to the preheating fires, is required; also there should be one man on the day shift for changing filters, cleaning dust flues, etc., and one man loading and unloading acid, etc. This, of course, does not include the men required for handling ore and running the roaster. Repairs are light in a well-designed and well-operated plant.

COMPARISON OF COSTS OF MANUFACTURING ACID IN CHAMBER AND IN CONTACT PLANTS.

For high-strength acid, such as is employed in the manufacture of dyes, explosives, and other special chemical industries, the contact process is by far the cheapest and most efficient.

For commercial oil of vitriol (66° B. acid), such as is usually shipped for various manufacturing processes, petroleum refining, and other uses, the contact process (excepting the "Mannheim" process) should produce the cheaper acid.

For low-strength acid, such as is usually employed in the manufacture of fertilizers, the acid itself, based on the cost of producing the SO_3 , can be made more cheaply by the contact than by the chamber process, but there are other factors to be considered, chief among them being the storage facilities and the necessity of diluting the

acid before using it. Furthermore, the chamber process as practiced at most fertilizer plants, does not require as highly trained and experienced a staff as does a contact plant. With an equally capable and trained staff the costs at some plants would probably show in favor of the contact process, but for the production of low-strength acid for ordinary purposes from pyrite or other ores which may contain impurities, the chamber process is the cheaper.

LEACHING AND SINTERING CALCINED ORE OR PYRITE CINDER.

In the discussion relating to the raw materials used for the manufacture of acid, mention is made of the fact that a large proportion of the Spanish pyrite ore, and also much of the domestic ore from the Southern States, carries copper in proportions that make its recovery worth while. Also, in order to prepare roasted or calcined ore, containing copper for the iron blast furnace, it is necessary to leach out the copper before sintering.

The method utilized to a large extent in the United States for the recovery of copper from calcined ore of low copper content (0.5 to 2½ per cent Cu) is commonly known as the Henderson salt leaching process. This process is ordinarily conducted in several distinct steps, and, while individual methods of carrying out these steps may vary, the steps themselves are practically the same in all practices. These may be characterized as follows: (1) Preparation of the charge, (2) roasting with sodium chloride, (3) leaching the calcine, (4) precipitation of the copper, and (5) disposal or treatment of the leached calcine.

PREPARATION OF THE CHARGE.

The charge usually consists of cold pyrite calcine, usually containing anywhere from 2 to 5 per cent sulphur; rock salt; and raw crushed pyrite. In some plants, however, no raw pyrite is used.

The method of preparing this charge varies considerably with different practices. In some plants the calcine and the rock salt are ground together in special grinders, such as Phillip MacLaren mills equipped with cast-iron slotted grates or screens; the ground product is of such fineness that more than 90 per cent of it will pass through a 10-mesh screen. It is inadvisable to grind too finely, as a certain proportion of coarse material should be present in order to facilitate free percolation of the leaching water in the subsequent treatment.

Other plants do not grind the material so finely. Some of the best plants in this country grind so that all of the material passes a ¾-inch square mesh and only about 80 per cent of it passes through a 10-mesh screen. Also, the practice of grinding the salt together with the balance of the charge is not followed at all plants, and

apparently is not necessary, as complete mixing is obtained on the roaster hearths later on.

The proportions of the various materials in the charge used also varies greatly according to individual practice. Some plants do not use any raw pyrite whatever, but a close study of the results obtained by various plants would seem to show that this practice is not conducive to the best results. If no pyrite is used a much higher temperature in the roaster is required, necessitating the use of a large amount of fuel and also frequently resulting, on account of the high temperature, in the formation of insoluble cuprous chloride. Judging from results, the best practice would seem to indicate the use of about $2\frac{1}{2}$ per cent of sulphur for each 1 per cent of copper present in the charge.

The calcine, raw pyrite, and rock salt are stored in separate bins, and are discharged from the bottom of these bins in carefully regulated proportions onto separate belt conveyors. These conveyors discharge onto a main belt, which therefore carries the finished charge in its correct proportions. As previously stated, in some plants this whole mixture is ground and screened. In other plants the grinding of the materials is done separately and the ground materials run to the bins that feed the individual conveyors. The complete mixed charge is carried by the main conveyor either direct to the feed hoppers above the salt roasters or else to a large storage hopper which supplies the feed hoppers.

ROASTING WITH SODIUM CHLORIDE.

There is considerable difference in opinion as to what reactions take place in the Henderson process. Some authorities maintain that there is a direct reaction between the sodium chloride and the copper salts present in the calcine, by which the copper salts are converted into soluble cupric chloride. However, the fact that a definite amount of sulphur apparently must be present for complete reaction would seem to indicate that nascent hydrochloric acid is formed by the reaction of sulphur dioxide upon the sodium chloride, and that this acid then reacts with the copper salts, forming soluble cupric chloride. Whatever the intermediate reactions may be, plant results indicate that a large proportion of sulphur is needed.

MUFFLE ROASTERS.

In this country the salt roasting is accomplished in several different forms of multiple-hearth roasters. Some plants use muffle roasters, such as the Wedge type. Muffle roasters are usually equipped with two coal furnaces, one on each side of the roaster. The hot furnace gases discharge into a vertical chamber extending the full

height of the roaster. The muffles are each divided into two sections; the hot gases from the vertical chamber enter all the muffles in parallel, by means of a separate inlet to each muffle. These inlets are provided with dampers for draft regulation. The gases discharge on the opposite side of a roaster into a stack, also connected with all the muffles in parallel.

The installation described refers only to half of each floor, as there are two muffles on each floor and similar heating equipment is installed on the other side of the furnace and heats the other half of the muffled floors in the same manner.

In order to obtain a greater heat efficiency, frequently a considerable number of bricks are removed from the lower floor of the muffles, thus allowing direct radiation of heat through the holes down onto the charge on the floor below. With a muffle roaster about 19 feet in inside diameter, having five hearths and a top drier hearth, and utilizing the upper four hearths as heating hearths and the bottom hearth as a cooling hearth, the capacity obtained is generally about 75 to 80 tons of dry calcine per day, provided the calcine does not contain more than 2 per cent copper. If the copper content of the calcine reaches 3 per cent, however, the capacity is reduced to about 50 tons daily, as a much longer roasting period is necessary to convert all the copper into soluble form.

When these roasters are operated in this way and no raw pyrite is used in the charge the temperature on the roaster hearth ranges from 750° to 1,100° F., and is preferably maintained around 1,000° to 1,050° F. If the ore temperature rises above 1,100° F., so-called ferrites are formed which are insoluble in water.

With such roasters operating on a charge consisting of about 85 per cent of calcine and 15 per cent of commercial rock salt by weight, and with no raw pyrite added, the fuel consumption, when coal is used, is about 10 per cent of the weight of the total charge put through the furnace.

SINGLE-HEARTH ROASTER.

Another type of roaster utilizing the same charge and the same temperatures is a large, single-hearth roaster equipped with four water-cooled rabble arms and heated by direct firing with fuel oil. This type of roaster consumes 15 to 18 gallons of fuel oil per ton of calcine roasted, and considerable difficulty is encountered from local overheating.

The hot calcine discharged from the roasters is allowed to stand in cans for a period of time limited by the number of cans available. It has been found that permitting the hot calcine to stand in closed cans causes the chloridizing to continue; therefore, if possible, this

material is allowed to stand for five hours or more before being dumped into the leaching vats.

The gases from this chloridizing roast are a mixture of combustion gases, hydrochloric acid gas, sulphur dioxide gas, and sulphur trioxide. These hot gases ascend through brick absorption towers countercurrent to a stream of water flowing down over the grill filling. The water is heated practically to boiling point, and the acid constituents of the gases are largely dissolved in the water, with the result that a hot solution of very weak acid is produced. This solution is run to storage and immediately used for leaching copper out of the roasted calcines; it has an acidity of about 0.3 per cent figured as HCl.

RAMEN-BESKOW MULTIPLE-HEARTH ROASTER.

Another method of chloridizing used at one plant in this country differs radically in the roasting equipment, roaster charge, and the way in which the heat is applied from the one just described. This method utilizes a chloridizing roaster known as the "Ramen-Beskow" roaster, which is about 18 feet inside diameter and has five hearths. The top hearth is provided with four arms and the other four hearths are each provided with two arms. The roaster has no steel shell, but is a thick brick setting about 20 feet square on the outside and circular on the inside, strongly reinforced with buck staves. The lower hearth is provided with four flues built into the four corners of the rectangular brick setting. The top hearth of the roaster is direct fired with producer gas from a coal-gas producer, and the products of combustion go to a stack: the heated ore passes through a lute into the second hearth, the gases discharging through the flues mentioned.

The average charge fed to this roaster is as follows: Dried calcine, 83 per cent; salt, 10 per cent; and pyrite, 7 per cent. The proportion of pyrite is varied somewhat from time to time, but the aim is to have at all times $2\frac{1}{2}$ times the sulphur in the mix that there is copper in the calcine. The copper content of the calcine varies considerably, but usually averages about $2\frac{1}{2}$ per cent.

The charge is heated on the top hearth to about $1,000^{\circ}$ F., so that when it discharges into the second hearth the oxidation of the pyrite content has started and chloridizing begun. Air for oxidation comes in through the bottom hearth, countercurrent to the descending charge, and ascends over the four lower hearths. The gases resulting from the oxidation— SO_2 , HCl, and some SO_3 —pass out of the second hearth into the flue in each of the four corners and are drawn downward through these flues by means of a fan and pass through three absorbing towers in series.

The first absorbing tower is 8 feet in inside diameter by 35 feet high. It is filled with tile with a little slag on top. Water flows down this tower countercurrent to the hot ascending gases and absorbs part of their acid content, discharging from the base of this tower as a weak acid with an acidity of 2 to $3\frac{1}{2}$ per cent figured as HCl. The gases then pass through the other two towers in series, but these towers are really scrubbing towers and the water from them is run to waste. The last of these two towers is packed with coarse limestone, which neutralizes any final acidity in the gases.

The average charge run through this roaster amounts to about 45 tons, dry weight, of calcine per 24 hours. About 3,000 pounds of coal per 24 hours is used in the form of producer gas to preheat the charge on the top floor of the roaster.

A concrete hopper bin is installed under the roaster into which the roasted calcine is discharged and in which it is permitted to accumulate for about 10 hours, when it is drawn off into cars and taken up an incline to a trestle, from which it is distributed to the various leaching tanks.

HERRESHOF MULTIPLE-HEARTH ROASTER.

A third method of chloridizing, which is used somewhat extensively in this country, is probably the most economical and efficient of any of the methods in current use.

The average charge run to the roaster is as follows: Salt, 7 per cent; raw pyrite, 3 per cent; and calcine, 90 per cent.

The roasting equipment consists of Herreshof roasters, each roaster being 22 feet in outside diameter and having seven hearths. Those roasters are lined with 4 inches of common brick and 9 inches of fire brick. The capacity of each roaster is about 50 long tons of total charge per day. No fuel is required and no preheating of the charge. The temperatures of the charge descending through the roaster are about as follows: Temperature on the second floor, 300° F.; on the fourth floor, 750° F.; and on the sixth floor, 550° F.

The material tends to cake solidly on the hearths, and the cakes must be barred out occasionally to prevent wearing off or breaking of the rabble teeth, but otherwise the roaster works well. The roasters are arranged in banks of three and are housed in a steel frame building with steel floors, in which ample room is allowed for barring out the roasters and taking care of operation and repairs.

The roasted material is discharged from the roasters into small, 1-ton hoppers, from which it is run into cars operated by a cable system, this system being in use throughout the plant. By means of this system the cars are run up on elevated tracks and dumped into the leaching tanks below.

COMPARISON OF THE DIFFERENT ROASTERS.

In reviewing the three principal methods of salt roasting, as described above, it will be noticed that they vary considerably, especially as regards the amount of salt used, the amount of pyrite used, and the fuel consumption. From practical plant results, it may be stated that by far the best results are obtained where the fuel consumption is either at a minimum or none is used and where the temperature on the roasting hearths is never permitted to exceed 750° to 800° F. There is a slightly added expense due to the increased amount of raw pyrite used, but this is far more than offset by the saving in fuel and in salt. The installation cost is somewhat greater, owing to the smaller capacity of the roasters.

LEACHING.

The hot product from the chloridizing roasters, after standing for a certain time, as previously mentioned, is leached with water that generally contains a small proportion of acid. Leaching is done in large vats or tanks, of which several different types are in use at various plants: also several different modifications are used.

A TYPE OF LEACHING PLANT.

One type of installation used rather extensively, and the details of its operation are as follows:

VATS.

Two types of leaching vats are used. The first and most satisfactory type consists of a double-walled, yellow-pine box about 11 feet square by 5 feet deep, inside dimensions. The outer box is built of 3-inch plain stock, and the inner box is of 3-inch stock with tongue and groove. The two boxes are doweled together with a space of about 3 inches between, which is filled with concrete, mixed in the proportion of 1 part of cement to about 4 of sand. The inner wooden box has no wood bottom: its sides extend to within 4 inches of the bottom of the outer box. The bottom is then covered with 7 inches of concrete, so the wooden sides of the inner box extend about 3 inches down into the concrete. Two tiers of brick grillwork are laid on top of the concrete. The first tier is of bricks, set on end and spaced to carry a second layer of brick laid flatwise. Cracks are left between the bricks in the second layer, and these cracks are filled with "salt hay" (dried salt-marsh grass), and a thin layer of the hay is strewed over the bricks. On top of this hay another layer of bricks is laid flatwise with cracks between, and salt hay is placed in the cracks and a little hay on top. A little cold, wet calcine is thrown on top of

the top layer of hay in order to prevent the hot calcine from burning it: about 8 tons of hot calcine is then dumped into each leaching box and leveled off roughly.

The best outlets for the copper liquor are large wooden blocks of yellow pine set into the side of the leaching boxes at the bottom. These blocks project through both the outer and inner boxes and are cemented into place by the concrete filling between the boxes. A hole is bored through this block and a taper wooden plug is used. This type of outlet is simple and lasts for years.

Another type of leaching vat is constructed of reinforced concrete and is about 16 feet square. The vat is fitted with the same type of grillwork as the wooden leaching boxes. This type, however, is not as satisfactory as the far cheaper wooden vat, for two reasons:

1. The concrete vats, although much more expensive to construct, are acted upon by the weak leaching acid and deteriorate rapidly. The steel reinforcing rods are also attacked and the whole installation, as regards economy of operation, has proved a disappointment.
2. For some reason not definitely known, the leaching capacity of the vats does not increase in the same ratio as the increase in size.

COPPER LEACHING PROCEDURE.

The charge of hot calcine is first leached with the second leaching water from a previous charge; this water, of course, already contains some copper. The water for the first leaching is not very warm, but is soon heated by the hot calcine.

The first leaching is permitted to stand for about five hours, when a large part of the copper in the ore is in solution. The plug is then withdrawn from the discharge hole of the vat, the leaching water—now at its highest strength in copper—is filtered off and is run through a series of settling tanks in order to settle out lead salts, etc., after which the liquor is run through the copper precipitating boxes. The strong liquor emerging from the leaching vats will average in gravity 6° to 14° B., and will contain 0.8 to 1 per cent of copper.

After the first leaching water has drained down to the level of the top of the calcine in the leaching vat, hot acidulated water from the roaster-gas absorbing towers is run into the vat at a rate sufficient to keep its level just above the calcine level, while the strong copper liquor is being discharged from the bottom of the leaching vat.

Tests are now made from time to time by sticking a bright steel "knife" down into the leached ore. If any soluble copper remains, the bright steel will immediately be covered with a coating of copper. Leaching with fresh hot acidulated water is continued until the "knife" test shows no soluble copper remaining.

When the leaching liquor being discharged from the bottom of the vat reaches a fairly low concentration in copper it is turned to storage and used for the first leaching of subsequent batches of fresh calcine.

SETTLING OF SOLUTIONS.

The strong liquor from the first leaching of the ore is run through an extensive system of wooden settling tanks, where lead salts and other impurities are precipitated as sludge. These settling systems are in duplicate and one system is drained and the sludge cleaned out while the alternate system is being used.

ANOTHER TYPE OF LEACHING EQUIPMENT.

Another type of copper-leaching equipment and its method of operation may be described as follows:

The leaching tanks used are circular wooden tanks 20 to 25 feet in diameter by $4\frac{1}{2}$ feet deep. These tanks are very heavily banded, the bands being kept away from the wood sides of the tanks themselves by means of 1-inch wooden blocks. The tanks are lined with a $4\frac{1}{2}$ -inch lining of "duro" brick, set in "duro" cement. The bottom of the tank is covered with a layer of what might be termed an asphalt mixture with a cement layer on top, the whole resembling bituminous pavement. The object of using the brick lining is to prevent burning of the wooden walls by the hot calcine. The bitumen bottom seems to protect the wooden staves below and to fill any shrinkage cracks caused by the heat of the charge above.

The liquor outlet of these tanks consists of a capped wood block built into the sides of the tank close to the bottom. No grill work of brick or tile is placed in these tanks, but they are filled to a depth of about six inches with chunks of coarse slag. On top of this is put about four inches of slough grass or excelsior, and about six inches of calcine is left on top of this grass or excelsior at all times. This type of filter bottom has proved very satisfactory; the liquor drawn off through it is extremely clear and such a bottom lasts a long time without replacement. In this connection, however, attention is called to the fact—which is brought out later—that an extremely large amount of wash water is required in order to free the calcines from the copper liquors. As this is not the case in other plants where the leaching tanks are smaller and where the more porous and uniform filter bottom is installed, it is extremely likely that uniform percolation is not attained, hence a much larger amount of wash water, or displacement water, is required.

The capacity of the 20-foot diameter tanks is about 45 tons of calcine, and of the 25-foot tanks, about 60 tons. This charge makes a bed with a total thickness of approximately $3\frac{1}{2}$ feet. The total

time of leaching for each tank is 24 to 48 hours. The first leaching is with final wash liquor from previous batches of ore. The liquor is cold but is rapidly heated by the hot calcine to nearly boiling temperature.

The liquor from the first leaching usually averages 3 to $3\frac{1}{2}$ per cent copper, but so much water is required to remove all the soluble copper that the average copper content of the liquors sent to the precipitating tanks is not more than $1\frac{1}{2}$ per cent. The amount of wash water varies greatly. It is probable that complete recovery of the soluble copper with the use of far less wash liquors could be accomplished by paying specific attention to three points:

1. The depth of ore bed is too great for maintaining uniform consistence throughout, and as a result the displacement of the heavy copper liquors downward by the lighter wash liquors will not be uniform, but will be governed largely by the density of the charge at individual places in the tank. Almost identical conditions are met with in the displacement of the acid from guncotton after nitration; in the Thompson displacement system, it has been definitely proven that such displacement with a sharp break between the heavier liquors below and the light liquors above can not be maintained beyond a certain well-defined depth of charge. The same thing has also been definitely proven in the displacement of cyanide liquors in current Western practice.

2. The size of the tank undoubtedly also governs the uniformity of displacement over any given cross section. This also has been demonstrated in acid displacement from guncotton, and has likewise been observed in other plants utilizing the Henderson process for copper leaching. Operators of these plants have discovered that with a smaller tank they can accomplish complete displacement of the copper liquors with the use of far less wash water.

3. The manner of adding the wash water has undoubtedly a decided effect upon the amount required for complete washing. If the original liquors be allowed to sink below the surface of the ore before the wash water is applied, cracks will develop in the ore and channeling will take place with any subsequent wash water added. When the main liquors have reached practically the top of the ore the wash water should be floated on quietly, and great care should be taken that it does not agitate the heavy liquors below, nor stir the ore. Otherwise mixing is bound to occur, and the washing resolves itself into simply a dilution process.

The concentrated copper solution is run through large wooden storage tanks and the weaker wash liquors are run to other wooden storage tanks, and, as previously stated, are reused for the first leaching of new batches of ore.

The tanks are allowed to drain until no more liquor will run off, then the leached calcine is transferred from the tanks by means of a locomotive crane with a clam-shell bucket, into gondola cars and transported to a bin from which it goes to the sintering plant.

A THIRD TYPE OF LEACHING EQUIPMENT.

Still another leaching outfit, which has given good results, and the method of operating it are as follows:

The leaching tanks are circular, 25 feet in diameter by 5 feet deep. These tanks are arranged in two parallel rows, each tank being elevated about 8 or 10 feet above ground level. The tanks are not brick lined, as the leaching water is put in first and the hot, roasted calcine dumped into the water, this procedure doing away with any chance of burning the wooden walls. The first layer of the filter bottom is 2-inch by 4-inch grillwork; on top of this, 4-inch by 4-inch timbers are laid parallel to each other and on their corners and are spaced about one-fourth to three-eighths of an inch apart in the clear. The corrugations formed by these timbers are filled with coke. A layer of anthracite culm is spread over the top and shoveled off each time with the leached calcine. As this culm can be used for fuel in sintering there is no loss in this procedure, and a fresh, open filtering medium is obtained with each new tank charge of calcine by this method of operation. In the bottom of each tank there are four square openings, through which the ore, after leaching, is shoveled into cars on tracks below. These openings are closed by beveled wooden plugs. The four openings are at the four corners of a square and are placed symmetrically in the rows of tanks so that all the openings come directly over the tracks below. Two tracks run under each tank, and are equipped with the Hunt cable system, by means of which, also, the leached material is transported to the sintering machine storage.

The capacity of each tank is 125 long tons of material.

The material is given three leachings. The first leaching is with the liquor from the second leaching of the previous charge. This liquor already averages about 1 per cent copper, and after the charge is leached will contain $2\frac{1}{2}$ to 3 per cent copper, at which strength it is drawn off and sent to the precipitating tanks. The second leaching is with liquor from the third leaching of the previous charge. This liquor averages about 0.2 per cent copper to start with, the copper content being increased to about 1 per cent by the second leaching of the calcine. The charge is leached a third time with water which, as stated above, analyzes about 0.2 per cent copper after the third leaching is finished. Ample storage for all these various strengths of leaching liquors is provided.

As previously stated, the liquor for the first leaching is drawn into the leaching tank in correct amounts and the roasted calcine is dumped into the liquor, thus removing the necessity for brick or other lining of the tanks to prevent injury from the hot calcine. The charge fills the tanks to within 6 or 8 inches of the top.

All transferring of the leaching liquors is performed by means of sump tanks and air lifts.

COPPER PRECIPITATION.

The precipitation of the copper from the solutions is done entirely by means of scrap iron. Electrolytic precipitation of such solutions is interfered with seriously by the presence of sodium sulphate, chlorides, and other salts in solution and is commercially impracticable. Various types of precipitating tanks or vats are used, according to the individual ideas of different designers.

One type of tank is constructed exactly similar to the double-wall concrete-lined tank, previously described as being used in certain plants for the leaching of the calcine, with the exception that it has no brick grill, but a grill work of wooden ties spaced several inches apart and supported on two ties laid on opposite sides of the bottom of the box. The scrap iron is placed on top of this wooden grill. After copper deposition has taken place for some time the scrap iron is shaken by hand, which causes the copper cement to fall off and drop down between the grills into the space below. Any type of old iron is used, but old galvanized iron is preferred, as it is not so badly rusted. The actual consumption of iron is about 110 pounds of scrap to 100 pounds of copper. The copper cement will average about 80 per cent copper.

Another type of precipitation apparatus which is widely used is large circular wooden tanks, each tank being about 22 feet in diameter by 5 feet deep and having no grill work at the bottom. These tanks are filled with scrap iron and are then run full of concentrated copper solution from the leaching tanks. The solution is agitated with air from time to time, also the scrap iron is picked up and shaken with the clamshell bucket of a locomotive crane at frequent intervals to free the adhering copper cement from the scrap iron. This is done until the liquor in the tank shows no more copper content, then the liquor is allowed to drain off through a filter and a fresh charge of liquor is added. The same procedure is followed with this charge of liquor and each succeeding charge until the depth of copper cement in the tank is about 18 inches. The residual scrap iron is then transferred by means of the crane to an adjacent tank. The copper cement is then dug out of the tank

by hand and is screened through a heavy screen of about one-fourth inch mesh. All the fine copper cement that passes through the screen is then run down into blister copper in a small reverberatory furnace; the rejects on top of the screen are put back into another precipitation tank, as these rejects consist largely of iron. The copper content of the cement averages about 85 per cent, and after treatment in the reverberatory furnace about 98 per cent.

Still a third type of tank, which has been successfully used, is a simple circular wooden tank about 12 feet 6 inches in diameter by $4\frac{1}{2}$ feet deep. No agitation is used in these tanks, but the contents are warmed at first with steam. About 10 to 14 hours are usually required for the complete precipitation of a tank full of strong solution.

The copper cement is shoveled out and transferred in wheelbarrows or buggies to screens where all large particles, iron and steel scraps, etc., are screened out. The screened cement will run about 70 per cent copper.

DISPOSAL OR TREATMENT OF LEACHED CALCINE.

With the exception of a small amount of extremely pure leached iron pyrites, known as "blue billy," which is used as a pigment in metallic plants, all of the material after leaching is either nodulized or sintered and sold as iron ore to blast furnaces.

NODULIZING EQUIPMENT AND METHOD OF OPERATION.

In the nodulizing of calcine an ordinary rotary cement kiln is used, generally about 7 to 9 feet inside diameter and 100 to 125 feet long. This kiln is set at the usual angle of an ordinary cement kiln and it is generally fired with powdered coal: the amount used varies usually between 14 and 15 per cent of the weight of the nodulized calcine output. The coal used is special gas coal, which generally runs about 35 per cent volatile matter, 51 per cent fixed carbon or higher, and the balance ash.

Some plants experience much trouble with the formation of "rings" in the kilns, whereas other plants operating on the same type of calcine have no trouble whatever. Careful investigation would seem to indicate that this trouble is caused by running at too high a temperature, and apparently the margin of safety between the temperature sufficient for correct nodulizing and the temperature at which serious "ring" formations will take place, is very small. A temperature in the combustion end of the kiln of around $2,000^{\circ}$ F. will result in a good product of nodulized calcine and no "ring" formation, whereas a temperature of $2,200^{\circ}$ F. results in serious "ring" formation, using the same calcine. This definite temperature would undoubtedly vary with different grades of calcine.

The hot nodulized calcine discharged from the kiln is sometimes permitted to drop into a pit where it is sprinkled with water, after which it is raised into storage bins by means of chain and bucket elevators. A possibly better form of disposal, however, consists of discharging the hot nodulized calcine into a chute, which in turn discharges into a cooling cylinder. This cylinder is 5 feet inside diameter and 60 feet long, and has a steel shell lined with flat segments of cast iron, which protects the steel shell from wear and can be easily renewed. The cylinder rotates in the same manner as does the kiln. The incoming hot nodulized calcine is partly cooled by spraying with water, and the cooling is completed by radiation through the walls of the cylinder and by evaporation as the material moves through it. Just enough water is added so that it will evaporate completely before the material is finally discharged.

The capacity of a nodulizing kiln 7 feet inside diameter by 100 feet long is about 150 tons of finished material a day, and of one 9 feet in diameter by 125 feet long, about 200 tons.

Some companies do not screen the fines from the nodulized product, as no objection to fines is raised by the blast furnaces that utilize the product, whereas other companies do and return the fines for renodulizing to the upper end of the kiln.

SINTERING EQUIPMENT AND METHOD OF OPERATION.

The sintering of leached calcine in order to produce a material suitable for use in iron blast furnaces is generally done by means of a Dwight-Lloyd type of sintering machine. These machines are usually constructed much heavier than those used for other metallurgical materials. A detailed description of their construction and operation is not necessary here.

The sintered material discharged from the machine is run over a grizzly and the fines are returned to a hopper and fed onto the sintering-machine pallets immediately in front of the calcine charge. This results in the pallet being covered with a thin layer of fairly coarse material which keeps the pallet from plugging and greatly increases the efficiency of the machine. This layer agglomerates easily with the charge above it, and does not have to be heated to as high a temperature as is required for sintering the main part of the charge. Thus the pallets are protected from overheating to a considerable extent.

The sintered material is usually discharged, after screening, directly into concrete or brick lined steel cars and drowned in these cars with an excess of water.

The fuel consumption, calculated as carbon, usually is anywhere from 7 to 10 per cent of the weight of the calcine; the fuel used is

either finely crushed coke or anthracite coal. In addition, 0.5 to 1 gallon of fuel oil, or a corresponding amount of gas, is generally used per ton of sinter for ignition of the charge.

The weight of the finished product is, as a rule, approximately 90 per cent of the dry weight of the calcines treated.

The requirements of the product for use in the iron blast furnace are a minimum of fine material, absence of vitrification, and the existence of a porous condition described as "cellular," which permits the furnace gases to permeate throughout the material.

Under normal 1913 price conditions, a complete Dwight-Lloyd plant of one standard machine would cost about \$20,000 and a complete plant of two standard machines about \$30,000. The capacity of each machine is about 150 tons per day.

PRESENT INSTALLATION COSTS.

The actual cost of erecting a leaching plant varies greatly, depending on plant design, climatic conditions at the plant locality, size of plant, and other factors.

Based on construction costs as of 1917-18, it may be stated that a complete plant, including a sintering installation having a daily capacity of 300 to 400 tons, will cost approximately \$2,500 per ton of calcine daily capacity. This cost would be divided approximately as follows:

Storage, crushing, drying, screening, mixing, tracks and transport facilities.....	\$400
Roasting	1, 150
Leaching.....	400
Precipitating (on basis of 2½ per cent metallic copper in calcine).....	200
Sintering.....	350
Total.....	2, 500

In a smaller plant—say of 50 tons daily capacity—the unit installation cost is considerably greater and for the same conditions as above would be about \$3,200 per ton of daily capacity.

If a nodulizing machine is used instead of a sintering machine, the cost of such nodulizing installation complete will be about \$600 per long ton of leached calcine in daily capacity; but it should be borne in mind that a nodulizing installation can not be economically operated on a capacity of less than 125 long tons of leached calcine a day.

The operating costs vary greatly according to different methods of operation, varying capacities, local costs of labor, fuel, etc.

In a large plant having a daily capacity of 250 to 500 short tons of calcine, the costs under conditions as of 1917-18 are approximately as follows:

Treatment of calcine (not including nodulizing or sintering), \$5.00 to \$8.90 per short ton of calcine.

Sintering, \$1.80 to \$3.60 per short ton of sintered material.

Nodulizing, \$1.40 to \$1.85 per short ton of nodulized material.

These costs include all charges for operation and repairs, plant amortization, taxes, and all company overhead and administration charges, also freight on incoming materials and sales costs.

USE OF NITER CAKE.

Niter cake is an impure acid sulphate or bisulphate of soda carrying a variable excess of sodium sulphate, or infrequently, of sulphuric acid from "niter pots" improperly charged or prematurely drawn. Pure sodium bisulphate (NaHSO_4) contains the chemical equivalent of 40.6 per cent sulphuric acid with 59.4 per cent sodium sulphate. Niter cake may occasionally have approximately the same composition as sodium bisulphate, but its acidity usually ranges between 28 and 44 per cent sulphuric acid. In addition, the cake contains small percentages of iron, aluminum, and silica as regular impurities, with arsenic, sodium nitrate, or nitric acid as accidental impurities.

The following is a typical analysis of niter cake:

<i>Typical analysis of niter cake.</i>		Per cent.
Silica		0.10
Oxides of iron and aluminum		.45
Free acidity		34.55
Sodium nitrate		.05
Sodium sulphate		64.25

In solution, niter cake breaks up into sodium sulphate and free sulphuric acid entirely available as such. Thus, 1 pound of niter cake with a free acidity of 34.55 per cent is equivalent to 0.44 pound of 60° B. sulphuric acid.

Niter cake is very deliquescent and if left in the open is gradually washed away and is wasted. The shipping of niter cake is rather a difficult problem, as the acid in the material corrodes bolts, nuts, and rods in the car bottoms, and the drip from the deliquescent cake attacks the springs and trucks.

The following is a list of manufacturing processes in which niter cake is being used or has been used successfully: Pickling iron or steel for galvanizing and tin plating, manufacture of hydrochloric acid, recovery of grease from wool suds and sewage, recovery of glycerin from soap lyes, precipitation of synthetic phenol, manufacture of epsom salts, regeneration of rubber, scouring in the process of calico bleaching, manufacture of carbon dioxide for mineral waters, and manufacture of glue and manure from leather scrap.

Experiment has shown that it is practicable to manufacture both superphosphate and sulphate of ammonia with niter cake, which use may greatly extend the consumption of niter cake in this country. At the present time the principal uses for niter cake are in the manufacture of hydrochloric acid and in pickling iron and steel.

Cleaning iron and steel with niter cake does not differ essentially from pickling with acid, but it introduces certain necessary manipulations due to the presence of sodium sulphate in large proportions as a diluent. Also, as a result of the inhibiting action of the sodium sulphate, it is necessary to allow a longer period to get the same results as when using acid. The usual procedure is to use part niter cake and part acid.

The manufacture of hydrochloric acid for metallurgical purposes is usually carried out on hearths on which sodium chloride mixed with ground niter cake is roasted under conditions that yield hydrochloric acid and neutral sodium sulphate.

LIST OF PUBLICATIONS RELATING TO SULPHUR AND SULPHURIC ACID.

A limited supply of the following publications of the Bureau of Mines has been printed and is available for free distribution until the edition is exhausted. Requests for all publications cannot be granted, and to insure equitable distribution applicants are requested to limit their selection to publications that may be of especial interest to them. Requests for publications should be addressed to the Director, Bureau of Mines.

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PUBLICATIONS AVAILABLE FOR FREE DISTRIBUTION.

BULLETIN 133. Wet Thiogen process for recovering sulphur from sulphur dioxide in smelter gases, a critical study, by A. E. Wells. 1917. 66 pp.

TECHNICAL PAPERS 58. Action of acid mine waters on the insulation of electrical conductors, a preliminary report, by H. H. Clark and L. C. Ilsley. 1913. 26 pp.

TECHNICAL PAPER 149. Answers to questions on the flotation of ores, by O. C. Ralston. 1917. 30 pp.

TECHNICAL PAPER 198. Sulphur dioxide method for determining copper minerals in partly oxidized ores, by C. E. van Barneveld and E. S. Leaver. 1918. 12 pp.

PUBLICATIONS THAT MAY BE OBTAINED ONLY THROUGH THE SUPERINTENDENT OF DOCUMENTS.

BULLETIN 47. Notes on mineral wastes, by C. L. Parsons. 1912. 44 pp. 5 cents.

BULLETIN 98. Report of the Selby Smelter Commission, by J. A. Holmes, E. C. Franklin, and R. A. Gould, with reports by associates on the commissioners' staff. 1915. 525 pp., 41 pls., 14 figs. \$1.25.

TECHNICAL PAPER 26. Methods for the determination of the sulphur content of fuels, especially petroleum products, by I. C. Allen and I. W. Robertson, 1912. 13 pp. 5 cents.

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